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APPLICATION OF LIQUID-LIQUID EXTRACTION TO THE SEPARATION OF TANTALUM FROM NIOBIUM.

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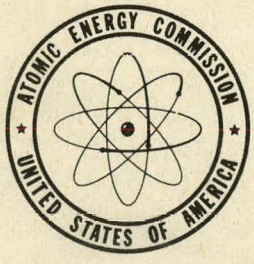

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APPLICATION OF LIQUID-LIQUID EXTRACTION TO THE SEPARATION OF TANTALUM FROM NIOBIUM*

by

Raymond A. Foos and H. A. Wilhelm

ABSTRACT

The use of liquid-liquid extraction for the separation of tantalum from niobium was demonstrated. Tantalum and niobium spectrographically free of each other were prepared in quantity on a continuous basis.

A tantalum-niobium mixture which contained about equal weights of each was obtained by processing a columbite-tantalite ore. An aqueous solution, or stock solution, containing the equivalent of 517 grams of tantalum and niobium pentoxides per liter was prepared by dissolving the hydrated oxides in excess hydrofluoric acid. Single stage extractions of this stock solution or its water dilutions with many organic solvents indicated that some solvents extracted more than 50 per cent of the total tantalum analyzing less than one per cent niobium. Although the ketones were most effective for obtaining this separation, many alcohols, amines, aldehydes, ethers, esters, organic phosphates, organic phosphites and mixed organic solvents were also useful. A multiple-contact batch extraction of the diluted stock solution carried out with diethyl ketone gave in three stages a 99 per cent recovery of niobium spectrographically free of tantalum and a 96 per cent recovery of the tantalum which analyzed about 0.15 per cent niobium. The most effective separation of tantalum from niobium was obtained when the free hydrofluoric acid content was low.

Other less corrosive systems were investigated for separating tantalum from niobium by liquid-liquid extraction. Extraction of hydrofluoric acid solutions of niobium and tantalum, which had been partially or completely neutralized with aliphatic or aromatic hydroxyamines, indicated favorable mass distribution and separation of tantalum from niobium. Tantalum preferred the organic phase in these systems. Although the same general extraction trends were observed for the amine-free and the amine-neutralized hydrofluoric acid solutions of niobium and tantalum, the former system gave higher degrees of separations. Niobium was preferentially extracted by the organic phase from a potassium hydroxide solution of niobium and tantalum. However, in this system the mass transfer and degree of separation was low.

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*This report is based on a Ph.D. thesis by Raymond A. Foos submitted July, 1954 to Iowa State College, Ames, Iowa. This work was done under contract with the Atomic Energy Commission.

Several countercurrent multistage extractions were carried out in which diethyl ketone was employed as the organic phase and the amine-neutralized hydrofluoric acid solution of niobium and tantalum as the aqueous feed. In from 10 to 15 stages, tantalum and niobium spectrographically free of each other were obtained quantitatively on a continuous basis.

The liquid-liquid system presented here indicated further the applicability of solvent extraction for separating inorganic compounds. Much of the information from this work is directly applicable to practical separation problems and therefore should be readily adaptable to specific laboratory and industrial scale operations.

INTRODUCTION*

Liquid-liquid extraction is becoming widely used for the separation of inorganic salts in industrial as well as in laboratory processes. Consequently, this technique was investigated as a method for the separation of some inorganic salts which are of current interest to the Atomic Energy Commission.

In general, a number of liquid-liquid systems containing niobium and tantalum salts were investigated. Various compositions of the aqueous phase were contacted with a variety of partially immiscible organic solvents in single stage extractions until equilibrium was obtained. Analyses of the equilibrium phases allowed calculation of the individual distribution coefficients, mass transfers from the aqueous phase to the organic phase and separation factors for each case. These equilibrium data afforded a method whereby the separation effectiveness of various liquid-liquid systems were compared. From the single stage data the range of the optimum operating conditions was estimated for a separation by a multistage extraction. These conditions were tested in a multiple-contact countercurrent extractor employing as many as 20 equilibrium stages. A few multistage extraction experiments were usually required to obtain the most effective separation conditions.

The aqueous feed was usually a mineral acid solution containing the niobium and tantalum salts to be separated although basic media in some cases were also investigated. Such variables in the aqueous phase as pH, acid concentration, salt concentration, complexing agents and salting-out agents were investigated. For the organic phase factors such as acidity, complexing agents, diluents and type of organic were found to be important in making separations. Relative volumes of the organic and aqueous phases were also varied to obtain separation data. Since separation of these salts on a commercial scale is desired, the economics of a process was an important factor in evaluating the practicability of a liquid-liquid system.

It was found that niobium and tantalum spectrographically free of each other could be produced on a continuous basis by a multistage extraction. The use of liquid-liquid systems for separating these inorganic salts proved useful on a laboratory scale. In a few cases the operations were scaled up to pilot plant production where they proved equally satisfactory.

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*Editors Note:

This introduction was written for a series of reports dealing with a number of liquid-liquid systems employed in separation studies. Only one of these systems is treated in this report. The other systems, including zirconium from hafnium and yttrium from rare earths by liquid-liquid extraction, are treated in Reports ISC-693 and ISC-695.

General History of Niobium and Tantalum Separation

In 1801 Hatchett discovered tantalum and niobium (or columbium) in a Connecticut mineral(1). Columbite and tantalite ores, the chief source of these elements, are ordinarily oxides which contain considerable amounts of iron, manganese and titanium. The columbite ores are richer in niobium while tantalite minerals contain more tantalum than niobium. Much of the world's supply of these ores is mined in Australia and Africa. Many minor deposits of these minerals have been located throughout the world.

Recently niobium and tantalum have become very useful in the field of metallurgy. Steels containing niobium or tantalum are very hard and quite chemically resistant. Niobium and tantalum metals resist the action of most acids except hydrofluoric acid. Because of their wide possible industrial applications a cheap method for recovering them from their ores is desired. Many methods have been reported for this recovery and for the separation of the niobium from the tantalum. Generally the procedures have been inadequate for low cost large scale production of pure niobium and tantalum compounds.

Several investigators have reviewed the various methods for separating niobium and tantalum salts up to about 1945 (1-3). The most widely investigated technique entails either fractional crystallization or precipitation. In the method of Marignac (1), niobic and tantalic acids were dissolved in a minimum amount of hydrofluoric acid. After saturating this solution with potassium fluoride, it was partly evaporated and cooled. This resulted in crystallization of potassium fluotantalate, K_2TaF_7. Further evaporation and cooling also yielded potassium pentafluoniobiate, $K_2NbOF_5 \cdot H_2O$. One gram of the tantalum salt dissolves in about 200 grams of water while an equal weight of the niobium compound requires only 12 parts water. Schoeller has devised a method of separating tantalum from niobium by fractionally precipitating their oxalates with tannin (4,5). Tannin precipitates the tantalum complex from a slightly acid solution while an excess of tannin precipitates niobium from a neutral solution. Although this technique has been quite useful as an analytical method for separating these elements, it does not appear to be practical on a large scale.

Recent attempts for separating tantalum from niobium by fractional precipitation have been reported. The use of tannin with cinchonine, strychnine or brucine to obtain the separation has been reported (6-8). Repeated precipitations of a hydrofluoric acid solution of the niobium-tantalum mixture with ferroin yielded pure tantalum (9). Fowler (10) fractionally precipitated tantalum at a pH of from 4.5 to 5 from their oxalic acid solution by slow hydrolysis of urea. After fusing the combined niobium and tantalum oxides with a mixture of potassium or sodium nitrates, chlorides or carbonates and potassium hydrogen

phosphate, it was reported that tantalum containing a small amount of niobium could be leached from the residue by a 0.02 normal oxalic acid solution (11). It has also been reported that potassium iodate precipitates tantalum but not niobium (12). Golibersuch and Young (13) produced niobium containing less than 0.2 per cent tantalum by fractionally precipitating niobium from a concentrated sulfuric acid solution while Wernet (14) reported that niobium and tantalum could be separated by crystallizing from a saturated hydrochloric acid solution.

Distillation of niobium and tantalum salts as a method of effecting their separation has been reported by several investigators (15-20). Cuvelliez (15) reported that niobium was separated from tantalum by roasting the ore in air at about 800 to 1200 degrees Centigrade with a basic substance which was usually calcium oxide. The residue from this roasting process was heated in a chlorine atmosphere at 800 to 1050 degrees Centigrade for several hours. Under these conditions 70 to 80 per cent of the niobium was volatilized as the chloride or oxychloride while practically all the tantalum remained in the mixture. It has also been found useful by some investigators to preferentially reduce the niobium oxide with hydrogen before addition of chlorine gas (18-20). Kroll and Bacon observed that much more niobium oxide than tantalum oxide formed a nitride when the mixture of these oxides was treated with ammonia at 600 degrees Centigrade. When chlorine was passed over this partially nitrided mixture at about 500 degrees Centigrade niobium was fractionally distilled. In one test 88 per cent of the niobium oxide and less than 5 per cent of the tantalum oxide were removed as a chloride from a mixture initially composed of 47 per cent niobium oxide and 53 per cent tantalum oxide. Hiskey and co-workers (17) volatilized niobium and tantalum by treating the oxide mixture with a chlorinated hydrocarbon.

Several successful attempts have been reported for separating tantalum and niobium salts by preferential adsorption on cellulose (21,22) or alumina (23). These investigations were carried out on a laboratory or tracer scale. Burstall and co-workers (21,22) charged cellulose with a fluoride solution of niobium and tantalum and then elutriated this with methyl-ethyl ketone. The tantalum was quantitatively transferred to the methyl-ethyl ketone and was found to contain as little as 0.10 per cent niobium. Addition of hydrofluoric acid to the eluant was required to remove the niobium from the cellulose. At a pH of 6.4 activated alumina adsorbed all the niobium and some of the tantalum when their oxalate solution was eluted with a solution of ammonium oxalate (23).

Columns charged with ion-exchange resins have been found to be effective in separating tantalum and niobium (24-27). The anion-exchange method employing a mixed hydrochloric-hydrofluoric acid solution of niobium and tantalum indicated that tantalum was preferentially adsorbed (24,25). Elution of their hydrochloric acid solution yielded the

opposite trend (26). The niobium and tantalum obtained by these ion-exchange techniques were better than 99 per cent pure relative to each other. Gillis and co-workers (27) recovered 95 per cent of the niobium free of tantalum by one pass of their oxalic acid solution containing about equal weights of the two elements. It is apparent that the preparations of high purity niobium and tantalum on a small scale can be accomplished by employing adsorption and ion-exchange techniques.

The use of liquid-liquid extraction for separating niobium and tantalum has been reported by several investigators. Leddicotte and Moore (28) found that a solution of methyldioctylamine in xylene extracted about 99 per cent of the niobium and only about 0.8 per cent of the tantalum from an 8.0 molar hydrochloric acid solution. Niobium and tantalum dissolved in nitric acid was not extracted by this organic phase when the acid concentration was as great as 10.6 molar. Scadden and Ballou (29) reported a partial separation of niobium from tantalum by preferentially extracting niobium from a nitric acid solution of their oxalates into a 0.6 molar solution of di-n-propyl phosphoric acid in dibutyl ether. The above liquid-liquid extraction experiments were all carried out at niobium and tantalum concentrations of about one gram or less per liter.

Wilhelm, Kerrigan and Cass (30) reported that many organic solvents were capable of preferentially extracting tantalum from a hydrofluoric acid solution containing high concentrations of niobium and tantalum. Stevenson and Hicks (31) successfully separated tantalum and niobium by the preferential extraction of tantalum into di-isopropyl ketone from their aqueous solution which also contained hydrofluoric acid and another mineral acid. The other mineral acids employed with the hydrofluoric were hydrochloric, sulfuric, perchloric and nitric. The hydrochloric acid was reported to be most useful. The additions of these acids to the system increased the per cent of tantalum transferred to the organic phase although the relative changes in transfer varied with acid concentration. A niobium-tantalum separation factor of 880 was reported for extracting a nitric-hydrofluoric acid aqueous system. In one extraction series which was equivalent to two stages of extraction the aqueous product phase contained 98 per cent niobium and 2.0 per cent tantalum while the organic phase product was 99.5 per cent tantalum and 0.5 per cent niobium. The yields of the high purity niobium and tantalum were not given. However, all of the extractions of Stevenson and Hicks were carried out on aqueous solutions containing less than 2.5 grams each of tantalum and niobium per liter.

Experimental Details

Previous work in this Laboratory showed that certain organic solvents would preferentially extract tantalum from a hydrofluoric acid solution of tantalum and niobium (30). Although an excess of hydrofluoric acid

was always employed in this early work, the effects of varying the concentration of niobium, tantalum and hydrofluoric acid on the extraction were not generally studied. Consequently, in the present study several series of tests were carried out in which the effects of variable extraction conditions were investigated. A series of single stage and multistage extractions employing constant aqueous phase conditions was carried out to determine the effect of the composition of organic phase. Similarly for a constant organic phase, extractions were carried out for varying aqueous phase conditions. Since the solutions of niobium and tantalum containing free hydrofluoric acid react with glass, other systems were investigated. It was found that the addition of certain amines to the hydrofluoric acid solution of niobium and tantalum permits the prolonged use of glass equipment for these extraction studies.

Columbite-tantalite ore, mined in South Dakota, was the source of the niobium-tantalum mixture employed for this study. This oxide ore contained the equivalent of about 65 weight per cent of the combined tantalum and niobium pentoxides as well as appreciable amounts of iron, titanium, manganese, aluminum, silicon and tin. It was treated and purified by a caustic fusion followed by sodium hydroxide then nitric or hydrochloric acid leaches of the fusion product. The solid residue containing the niobic and tantalic acids, or earth acids, was then dissolved in aqueous hydrofluoric acid. Addition of concentrated hydrofluoric acid to the freshly prepared earth acids residue resulted in a niobium and tantalum solubility equivalent to about 530 grams of oxide per liter. However, a solution containing the equivalent of only 50 grams of oxide per liter was obtained when the hydrofluoric acid was added to calcined pentoxides of niobium and tantalum. About six or seven moles of hydrofluoric acid per mole of niobium or tantalum were required to obtain a stable fluoride solution of these elements. The niobium-tantalum fraction in this ore in terms of oxides consisted of about 52 per cent tantalum pentoxide and 48 per cent niobium pentoxide.

One stock solution of the niobium-tantalum-hydrofluoric acid mixture was prepared. Due to the corrosive nature of an acid fluoride solution it was made up and stored in polyethylene containers. Most of the tests were carried out directly on the stock solution or its various water dilutions. The total niobium and tantalum concentration of this stock solution was equivalent to about 517 grams per liter of the combined pentoxides. Based on the average of the molecular weights for niobium and tantalum pentoxides, this represents about a 1.45 molar solution. The total acidity or base equivalent of the stock solution was 17.3 moles per liter while its fluoride ion concentration was 15.3 equivalents per liter.

A large number of single and multistage extractions were carried out on this stock solution and its various water and amine solutions. A few single stage extractions were also made on an aqueous potassium hydroxide solution of niobium and tantalum. All the multistage extractions were

carried out in the countercurrent multistage extractor illustrated in Figure 1. The design, assembly and operation of this extractor has been discussed and illustrated by Wilhelm and Foos (32). For the single stage extractions of aqueous solutions containing considerable free hydrofluoric acid, polyethylene equipment was employed. However, when this acid concentration was low or amine was present glass equipment was used. Equilibrium in this system is approached quite rapidly so the liquids were mixed vigorously for only about 30 seconds. The equilibrium phases were separated and assayed.

The hydrated oxides (or hydroxides) of niobium and tantalum were precipitated from the organic and aqueous phases by addition of excess ammonium hydroxide. Acetone was usually added to these phases before precipitation to aid in filtering and recovering the niobium and tantalum compounds. After filtering, the hydrated oxides were converted to pentoxides by calcining at 800 degrees Centigrade for at least two hours. These pentoxides were assayed for relative niobium and tantalum content by x-ray fluorescence (33) and spectrographic analysis (34). The first method was employed for mixtures containing between 2.0 and 98 per cent niobium and was accurate to within ± 5 per cent. The spectrographic methods of Fassel and Krotz (34) was used for samples containing less than 2.0 per cent or more than 98 per cent niobium. The accuracy of the spectrographic methods in these high purity ranges was ± 10 per cent of the minor constituent. In all of the analytical results only the content of niobium and tantalum is considered. It is assumed that the total percentage of niobium oxide plus tantalum oxide equals 100 per cent. Since a qualitative analysis of the niobium-tantalum fraction which was used in preparing this stock solution showed that it contained only small amounts of impurities, these relative percentages should also be fairly accurate on the total oxide weight basis. All qualitative analyses were carried out spectrographically.

Potentiometric titrations of the stock solution and its various water dilutions with sodium hydroxide indicated that at a pH of 9, all the hydrogen ions were replaced by sodium. Consequently, the total acidity or base equivalent was determined by a direct acid-base titration using phenolphthalein as the indicator. Although the magnitude of this value may be somewhat connected with the niobium and tantalum content of the solution, it gives an indication as to the concentration of hydrofluoric acid in the system. Such data also aid in reproducing extraction conditions. This titration was also employed for determining the total acidity in many of the equilibrium organic phases which had been employed in the extractions.

Determination of the fluoride ion concentration in some of the aqueous and organic phases was also desirable for characterizing these solutions. The procedure developed by Willard and Winter (35) was

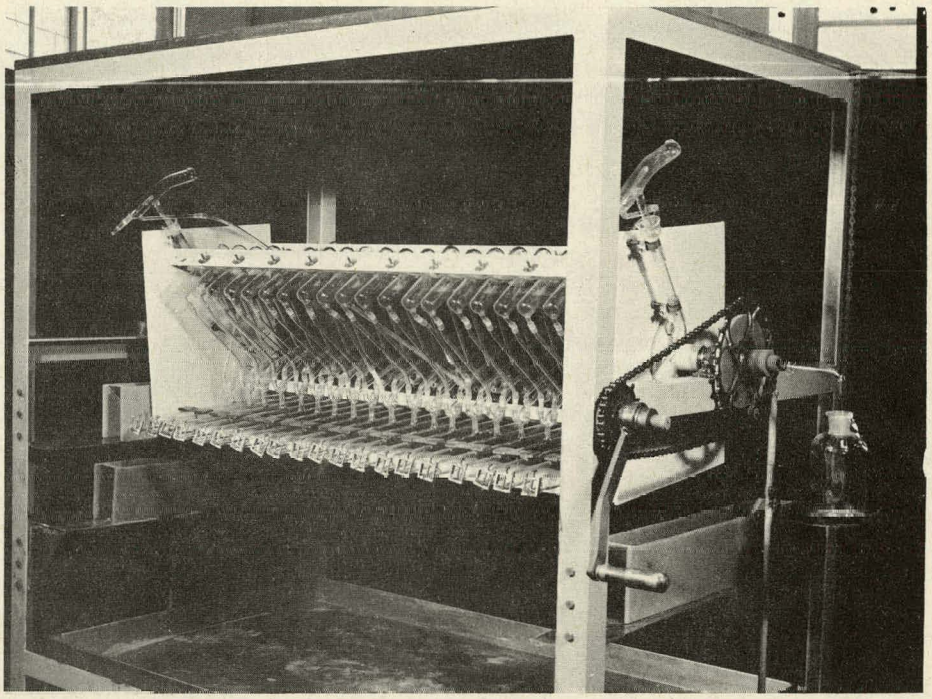

Figure 1. Twenty Stage Countercurrent Liquid-liquid extractor.

used for this analysis. The reagent solutions employed were:

No. 1. About 1.0 gram of zirconyl nitrate dissolved in 250 milliliters of water.

No. 2. About 1.0 gram of Alizarin red dissolved in 100 milliliters of ethyl alcohol.

No. 3. Standard thorium nitrate solution.

In carrying out this titration a known volume of a diluted fluoride solution was placed in a test tube. To this fluoride solution was added about two drops of a solution prepared by mixing three parts of solution number 2 with two parts of solution number 1. The pH of this fluoride solution should be about 2 to 4 for obtaining a sharp end point. Standard thorium nitrate was then added dropwise until a permanent pink coloration resulted. If the fluoride solution was not dilute, the thorium fluoride precipitate masks the color and obscures the end point.

This titration for the fluoride ion concentration was employed for many of the aqueous and organic phases containing niobium and tantalum. Ethyl alcohol instead of water, was used as a diluent for the organic phases. The fluoride ion concentration obtained by this titration for niobium-tantalum hydrofluoric acid solutions was always slightly lower than the corresponding value for total acidity. It is believed that this value for the fluoride ion concentration is another variable whereby the conditions in any hydrofluoric acid solution of niobium and tantalum can be reproduced.

Results and Discussion

Processing columbite-tantalite ore (36)

A laboratory scale procedure developed in the Ames Laboratory for processing this particular South Dakota columbite-tantalite ore to obtain its niobium-tantalum fraction employs for each batch about 10.0 grams of the finely ground ore. A caustic mixture consisting of 8.0 grams of sodium hydroxide and 4.0 grams of sodium peroxide is heated for 30 minutes at 650 degrees Centigrade in the presence of this ore. After cooling, the fusion product is leached with about 300 mililiters of hot 1.0 molar sodium hydroxide. The solution from this basic leach, which contains primarily aluminum, tin, manganese and silicon, is filtered and discarded. The residue is next leached with a hot solution of about 200 milliliters of 5.0 molar nitric acid containing a trace of hydrogen peroxide. The solution from this acid leach which contains primarily iron and manganese is filtered and discarded. A minimum amount of concentrated hydrofluoric acid is added to the residue to dissolve the earth acids. It requires

about 5.0 milliliters of the concentrated hydrofluoric acid to form a stable solution of the niobium and tantalum from the ore employed. The solution is recovered from the unreacted ore by decantation or filtration.

Table 1 indicates the weights of each fraction as oxides obtained from processing 10.0 grams of this columbite-tantalite ore.

Table 1

Weights of Various Fractions from Processing 10.0 Grams of a Columbite-Tantalite Ore

Fraction	Weight of oxide
1. Soluble in NaOH leach (ppt. with HNO_3-NH_4OH)	= 1.57 g.
2. Soluble in HNO_3 + H_2O_2 leach (ppt. with NH_4OH)	= 1.60 g.
3. Soluble in HF leach (ppt. with NH_4OH)	= 7.13 g.
4. Insoluble unreacted ore	= 0.32 g.
Total	10.62 g.

Some work to be described later was carried out with a potassium hydroxide solution of niobium and tantalum. This solution, which contained an equivalent of 65 grams of combined oxides per liter, was prepared by dissolving the earth acids obtained in step 2 of Table 1 in about two molar potassium hydroxide.

A qualitative analysis of the niobium-tantalum oxide fraction, which was precipitated from the hydrofluoric acid solution with ammonium hydroxide, indicated strong amounts of niobium and tantalum, weak amounts of silicon, tin, and titanium, very weak amounts of aluminum, iron and manganese and a trace of sodium. It can be seen from Table 1 that the ore used for this example contained about 67 per cent of the total as niobium and tantalum oxides. As reported above, about 52 per cent of this fraction was tantalum oxide and about 48 per cent niobium oxide.

Single stage extractions

Extraction of the stock solution or its water dilutions

A large number of single stage extractions were carried out employing the previously described stock solution or its various water dilution as the aqueous feed. All of these extractions employed equal volumes of the initial aqueous and organic phases. The data for these extractions which appear in Table 2 are classified according to the general class of organic solvent. Each organic class is subdivided alphabetically into its various compounds. The data for extraction with the mixed organic solvents are given in the last section of Table 2. For each single stage extraction the data include the composition of the organic phase, the per cent stock solution as aqueous feed, the analysis of the pentoxides recovered from the equilibrium organic and aqueous phases, the niobium and tantalum distribution coefficients, the tantalum-niobium separation factor, the mass transfer as oxide to the organic phase, and the per cent of total tantalum as oxide transferred to the organic phase. The per cent stock solution as the aqueous phase refers to its dilution with water. As an example, the 22 per cent stock solution aqueous phase means that 22 milliliters of the stock solution was diluted to 100 milliliters with water and then employed as the aqueous feed. It should be emphasized that in these data the niobium and tantalum oxide are assumed equal to 100 per cent. Errors in sample preparation and analyses probably explain why the data for three of the extractions showed slightly more than 100 per cent of the tantalum oxide to be recovered from the equilibrium organic phase.

The organic solvents employed for these niobium-tantalum extractions are listed in Table 2 and include alcohols, aldehydes, amines, esters, ethers, hydrocarbons, halogenated hydrocarbons, ketones, organic phosphates, organic phosphites, mixed organic solvents and a few miscellaneous compounds. In all cases, whenever there was transfer to the organic phase a considerable preference for tantalum was evident. This investigation showed that a great number of common water-immiscible organic compounds separate tantalum from niobium when these elements are together in a hydrofluoric acid solution.

As a general class the ketones appeared to be the most effective organic compounds for extracting pure tantalum and obtaining high tantalum-niobium separation factors. The data for the ketone extractions of the 22 per cent stock solution indicate that some of them extract appreciable quantities of high purity tantalum. Mesityl oxide, isophorone and cyclohexanone in one contact of this aqueous phase extracted about 94 per cent of the total tantalum. The amounts of niobium oxide in this tantalum as oxide were 0.2, 0.7 and 2.4 per cent, respectively, while the calculated tantalum-niobium separation factors were 4180, 3000 and 726, respectively,

Table 2

Single Stage Extractions of the Aqueous Stock Solution or Its Water Dilutions by Various Organic Solvents

Ext. no.	Organic phase	Aq. feed % Stock soln.	Equil. anal. % Ta_2O_5 Aq.	Equil. anal. % Ta_2O_5 Org.	K_{Ta}	K_{Nb}	Ta-Nb Sepn. factor	% total oxide weight in org.	% total Ta_2O_5 in org.
	A. Alcohols								
1.	Amyl alcohol(n)	22	27.7	95.8	1.67	0.0283	59	37.1	68.4
2.	Amyl alcohol(iso)	22	24.0	96.6	2.12	0.0234	91	38.1	70.9
3.	Amyl alcohol(tert)	22	11.4	84.8	4.66	0.107	44	56.5	92.1
4.	Benzyl alcohol	22	40.5	97.5	0.638	0.0114	56	24.5	45.9
5.	Butyl alcohol(n)	22	14.3	91.1	4.48	0.0727	62	50.3	88.3
6.	Butyl alcohol(iso)	22	16.4	91.4	3.90	0.0721	54	47.7	84.0
7.	Butyl alcohol(sec)	22	29.9	59.9	2.05	0.586	3.5	84.5	97.7
8.	Di-isobutyl carbinol	22	51.5	98.7	0.164	0.00235	70	8.1	15.4
9.	Heptanol-3	22	34.3	98.5	1.09	0.00845	129	29.5	55.9
10.	Methyl amyl carbinol	22	22.5	98.3	2.42	0.0119	203	39.0	73.8
11.	Methyl n-hexyl carbinol	22	31.3	98.6	1.30	0.00822	158	29.2	55.3
12.	Methyl propyl carbinol	22	15.8	95.8	4.08	0.0340	120	45.4	83.7
13.	Octyl alcohol(iso)	22	44.9	98.3	0.371	0.00534	70	18.7	35.3
14.	Oleyl alcohol	22	53.5	87.7	0.107	0.0175	6.2	5.9	10.0
15.	Pentasol-27*	100	15.2	89.5	3.86	0.810	48	50.6	87.0

*A mixture of isomeric amyl alcohols with the primary alcohols composing about 70 per cent.

Table 2 (Continued)

Ext. no.	Organic phase	Aq. feed % Stock soln.	Equil. anal. % Ta_2O_5 Aq.	Equil. anal. % Ta_2O_5 Org.	K_{Ta}	K_{Nb}	Ta-Nb Sepn. factor	% total oxide weight in org.	% total Ta_2O_5 in org.
	B. Aldehydes								
16.	Butyraldehyde(n)	100	42.0	98.6	0.607	0.00635	96	20.6	39.0
17.	Butyraldehyde(n)	25	42.9	99.7	0.530	0.00114	465	17.6	33.7
18.	Crotonaldehyde	25	10.3	95.4	8.89	0.0483	183	48.7	89.5
19.	Furfural	22	14.3	98.4	5.25	0.0147	358	45.6	86.3
20.	Heptaldehyde	25	53.5	I.S.	-	-	-	0.62	-
21.	Paraldehyde	25	49.5	98.4	0.237	0.00373	64	8.6	16.3
	C. Amines								
22.	Aniline	22	15.9	66.7	11.3	1.06	11	73.5	94.4
23.	Phenyl ethyl ethanolamine	22	48.8	81.0	0.647	0.145	4.5	20.9	32.5
24.	Toluidine(meta)	22	13.9	59.8	31.6	3.44	9.2	88.7	102
25.	Toluidine(ortho)	22	15.2	70.1	11.3	0.865	13.1	70.1	94.6
26.	O-Tolyl propanolamine	22	16.8	75.3	7.25	0.480	15	62.7	90.6
	D. Esters								
27.	Benzyl acetate	22	53.5	-	-	-	-	0	0
28.	n-Butyl d-tartrate	22	39.1	98.1	0.686	0.00856	80	26.2	49.3
29.	Diethyl carbonate	22	53.5	99.5	0.0123	0.0000906	136	0.63	1.21
30.	Diethyl oxalate	22	51.5	99.6	0.177	0.000557	210	5.48	10.5

I.S. = Insufficient sample.

Table 2 (Continued)

Ext. no.	Organic phase	Aq. feed: % stock soln.	Equil. anal.: % Ta_2O_5 Aq.	Equil. anal.: % Ta_2O_5 Org.	K_{Ta}	K_{Nb}	Ta-Nb Sepn. factor	% total oxide weight in org.	% total Ta_2O_5 in org.
	D. Esters (Continued)								
31.	Diethyl phthalate	22	52.5	99.4	0.0922	0.000557	160	5.10	9.82
32.	Ethyl acetoacetate	100	9.64	90.4	6.18	0.126	49	58.3	101
33.	Ethyl acetoacetate	50	12.4	94.7	5.71	0.0452	127	48.2	87.7
34.	Ethyl acetoacetate	22	19.6	97.1	3.52	0.0261	135	42.9	79.7
35.	Ethyl salicylate	22	53.9	-	-	-	-	0	0
36.	Methyl benzoate	22	53.5	I.S.	-	-	-	1.03	-
37.	Tributyl citrate	22	53.5	97.7	0.0440	0.00119	37	2.46	4.63
38.	Triethyl citrate	22	21.9	99.2	2.48	0.00535	464	38.1	72.7
39.	Tripropyl citrate	22	49.7	94.7	0.237	0.0131	18.1	11.7	21.3
	E. Ethers								
40.	Dibutyl ether	22	53.6	-	-	-	-	0	0
41.	Diethyl ether	100	6.24	96.4	11.2	0.0282	398	49.8	92.3
42.	Diethyl ether	22	44.8	98.7	0.426	0.00472	91	14.3	27.1
43.	Di-isopropyl ether	22	53.6	I.S.	-	-	-	0.46	-
44.	Diphenyl ether	22	53.5	-	-	-	-	0	0
45.	Methyl phenyl ether	22	53.5	-	-	-	-	0	0
	F. Ketones								
46.	Cyclohexanone	22	5.1	97.6	17.0	0.0223	762	50.1	94.0
47.	Diethyl ketone	100	7.24	96.8	8.33	0.0214	390	48.1	89.8

Table 2 (Continued)

Ext. no.	Organic phase	Ac. feed % Stock soln.	Equil. anal. % Ta_2O_5 Aq.	Equil. anal. % Ta_2O_5 Org.	K_{Ta}	K_{Nb}	Ta-Nb Sepn. factor	% total oxide weight in org.	% total Ta_2O_5 in org.
F. Ketones (Continued)									
48.	Diethyl ketone	80	7.06	97.2	9.16	0.0197	465	47.6	88.8
49.	Diethyl ketone	60	10.0	99.0	6.70	0.00766	874	46.4	88.3
50.	Diethyl ketone	40	17.2	99.6	4.04	0.00303	1335	43.6	83.4
51.	Diethyl ketone	20	24.5	99.87	2.52	0.00124	2040	38.3	73.7
52.	Diethyl ketone	10	31.4	99.93	1.61	0.000520	3100	32.6	62.7
53.	Diethyl ketone	5	38.4	99.96	0.9107	0.000205	4475	25.5	50.0
54.	Diethyl ketone	2.5	45.2	contamination	-	-	-	17.4	33.5
55.	Di-isobutyl ketone	22	54.6	99.3	0.208	0.000183	113	1.16	2.17
56.	Di-isopropyl ketone	100	26.4	98.8	1.60	0.00728	200	36.2	68.8
57.	Di-isopropyl ketone	22	41.8	99.89	0.504	0.000372	1350	18.4	35.4
58.	Heptanone-2	22	37.0	99.90	0.950	0.000545	1740	27.9	53.7
59.	Heptanone-3	22	48.4	99.90	0.345	0.000336	1030	14.9	28.6
60.	Heptanone-4	22	50.6	99.3	0.258	0.00177	146	12.1	23.2
61.	Isophorone	100	2.90	95.7	22.0	0.0297	740	51.5	95.0
62.	Isophorone	22	4.71	99.3	17.0	0.00565	3000	49.0	93.7
63.	Mesityl oxide	22	8.57	99.8	8.96	0.00215	4180	46.4	93.5
64.	Methyl ethyl ketone	100	12.4	78.3	5.65	0.222	25	62.8	93.2
65.	Methyl ethyl ketone	75	12.4	87.1	6.70	0.141	48	54.4	90.5
66.	Methyl ethyl ketone	50	13.9	88.7	6.49	0.133	49	51.9	88.5

Table 2 (Continued)

Ext. no.	Organic phase	Aq. feed % stock soln.	Equil. anal. % Ta_2O_5 Aq.	Equil. anal. % Ta_2O_5 Org.	K_{Ta}	K_{Nb}	Ta-Nb Sepn. factor	% total oxide weight in org.	% total Ta_2O_5 in org.
	F. Ketones (Continued)								
67.	Methyl ethyl ketone	22	15.9	93.6	6.70	0.0875	77	48.3	87.0
68.	Methyl n-hexyl ketone	100	30.3	99.1	1.27	0.00492	259	34.1	64.6
69.	Methyl n-hexyl ketone	22	40.0	99.87	0.645	0.000540	1200	21.2	40.7
70.	Methyl isobutyl ketone	22	24.0	99.1	1.95	0.00546	657	34.0	64.8
71.	Methyl isopropyl ketone	22	24.5	99.7	3.00	0.00304	990	43.7	84.2
72.	Methyl phenyl ketone	22	30.7	99.4	1.28	0.00335	382	31.1	59.5
73.	2,4 Pentanedione	22	26.8	98.2	2.56	0.0177	145	36.3	68.5
	G. Phosphates								
74.	Tributoxyethyl phosphate	22	5.79	95.4	14.7	0.0442	333	51.6	94.8
75.	Tributyl phosphate	22	1.68	95.4	53.1	0.0438	1200	53.2	97.6
76.	Tri-2-ethylhexyl phosphate	22	25.9	98.9	2.59	0.0117	222	42.7	81.0
	H. Phosphites								
77.	Di-2-ethylhexyl hydrogen phosphite	22	17.6	94.2	4.46	0.0586	76	48.8	88.4

Table 2 (Continued)

Ext. no.	Organic phase	Aq. feed % stock soln.	Equil. anal. % Ta_2O_5 Aq.	Equil. anal. % Ta_2O_5 Org.	K_{Ta}	K_{Nb}	Ta-Nb Sepn. factor	% total oxide weight in org.	% total Ta_2O_5 in org.
	H. Phosphites (Continued)								
78.	Tri-2-ethylhexyl phosphite	22	29.9	99.7	1.76	0.00204	865	38.5	73.9
79.	Tri-isooctyl phosphite	22	23.0	98.0	2.84	0.0172	166	45.1	85.0
	I. Miscellaneous								
80.	Carbon disulfide	22	53.5	-	-	-	-	0	0
81.	Chloroform	22	53.5	-	-	-	-	0	0
82.	Heptane	22	53.5	-	-	-	-	0	0
83.	Isoamyl nitrite	22	53.5	-	-	-	-	0	0
84.	Nitrobenzene	22	53.5	-	-	-	-	0	0
85.	Trichloroethylene	22	53.5	-	-	-	-	0	0
86.	Toluene	22	53.5	-	-	-	-	0	0
	J. Mixed Solvents								
87.	40% Acetone + 60% diethyl ketone	22	19.8	98.8	4.63	0.0140	331	41.8	79.5
88.	25% Acetone + 75% di-isobutyl ketone	22	53.5	99.0	0.0704	0.000816	86	2.75	5.2
89.	40% Acetone + 60% di-isopropyl ketone	22	37.4	99.7	0.991	0.00655	640	25.6	48.7

Table 2 (Continued)

Ext. no.	Organic phase	Aq. feed % stock soln.	Equil. anal. % Ta_2O_5 Aq.	Equil. anal. % Ta_2O_5 Org.	K_{Ta}	K_{Nb}	Ta-Nb Sepn. factor	% total oxide weight in org.	% total Ta_2O_5 in org.
J. Mixed Solvents (Continued)									
90.	25% Primene 81-T + 75% diethyl ketone**	22	1.51	60.6	288	2.88	100	88.7	103
91.	12.5% Primene 81-T + 87.5% diethyl ketone	22	1.13	83.6	129	0.292	443	65.0	104
92.	5% Primene JM-T + 95% diethyl ketone***	22	13.9	99.1	5.17	0.00750	1210	43.2	82.2
93.	25% Primene JM-T + 75% di-isobutyl ketone	22	2.26	81.3	55.7	0.349	159	65.9	103
94.	25% Primene JM-T + 75% heptane	22	13.9	79.7	8.35	0.342	24	60.8	95.0
95.	5% Primene JM-T + 95% heptane	22	43.7	97.9	0.409	0.0675	61	15.4	28.9

**A technical grade amine mixture of highly branched primary amines having a tertiary alkyl structure with the number of carbon atoms per molecule varying principally from 12 to 15.

***A primary amine similar in structure to Primene 81-T while containing essentially 18 to 24 carbon atoms per molecule.

for these organic liquids. It is apparent from these data that a two or three stage extraction process employing these solvents would yield quite pure tantalum and niobium with high recoveries of each.

Many other ketones extracted purer tantalum from the 22 per cent stock solution than was extracted by these three ketones. Although the purities were greater, the quantities of tantalum extracted were less. Heptanone-2 and heptanone-3 extracted about 54 and 29 per cent, respectively, of the total tantalum with a purity of 99.90 per cent. Di-isopropyl ketone extracted 35 per cent of the tantalum with a purity of 99.89 per cent tantalum oxide in the recovered oxide. About 74 per cent of the tantalum with a recovered oxide purity of 99.87 per cent was extracted by diethyl ketone while 84 per cent of the tantalum giving an oxide purity of 99.7 per cent was transferred into methyl isopropyl ketone. Methyl n-hexyl, methyl isobutyl (hexone) and methyl phenyl ketone (acetophenone) extracted 41, 65 and 60 per cent of the total tantalum, respectively, with recovered oxide purities of 99.1, 99.87 and 99.4 per cent tantalum oxide. Di-isobutyl ketone and heptanone-4 also extracted tantalum containing less than 1.0 per cent niobium although in small amounts. As is apparent from Table 2, the only ketones which did not extract tantalum with an oxide purity of 99 per cent or better from the 22 per cent aqueous stock solution was methyl ethyl ketone, 2,4 pentanedione and cyclohexanone.

Comparison of the data for the ketones above indicates that certain molecular structure features of an organic compound affects its extraction behavior. As a general rule, the lower molecular weight ketones in a homologous series transferred more tantalum. The purity of the recovered oxides was as good or better than the higher members of the series. From the data for methyl ethyl, methyl isopropyl, methyl isobutyl, methyl amyl and methyl n-hexyl ketone it is evident that the tantalum and niobium distribution coefficients and per cent mass transfers decreased with increased molecular weight of the organic. The purity of the recoverable tantalum in the organic phase remained above 99 per cent and the tantalum-niobium separation factor above 600 for all of these organic compounds except methyl ethyl ketone. Comparison of the data for dipropyl ketone (heptanone-4) and di-isopropyl ketone would indicate that the branched chain improves mass transfer and separation factor. The data for the 2, 3 and 4 heptanones indicate that as the keto group approaches the end of the chain the mass transfers and separation factors increase. The effect of unsaturation is illustrated by comparing the extractability of the tantalum by mesityl oxide (methyl isobutylene ketone) and methyl isobutyl ketone. It is apparent that in the presence of this double bond structure the amount and purity of the tantalum transferred to the organic phase were increased.

The data in Table 2 indicate further that a few pure organic solvents other than ketones extracted tantalum containing less than one per cent

niobium from an approximately 22 per cent stock solution. These organic compounds were diethyl carbonate, diethyl oxalate, diethyl phthalate, triethyl citrate, tri-2-ethylhexyl phosphite and n-butyraldehyde. However, the first three of these compounds each extracted less than 11 per cent of the total tantalum. The last three of these organic liquids extracted 73, 74 and 34 per, respectively, and it is apparent that only these compounds compared favorably with most of the ketones for obtaining high purity tantalum in high yields.

The alcohols as a general class of organic compounds yielded separation factor, distribution coefficient and mass transfer data which indicated that they could be employed effectively for separating niobium and tantalum. Generally the separation factors varied from 50 to 200 while appreciable material was extracted by the organic phase. In most cases the same general trends in regard to structure and size of the alcohol molecule were observed as reported for the ketones. As the position of the hydroxy group in secondary alcohols approached the end of the molecule, the tantalum-niobium separation factor and mass transfer increased. Secondary alcohols appeared to give better results than primary alcohols except for sec-butyl alcohol which was quite soluble in this aqueous phase. A comparison of the data for corresponding alcohols and ketones indicates that the alcohols gives somewhat greater mass transfers to the organic phase and considerably lower tantalum-niobium separation factors.

The few aldehydes that were used to extract this diluted stock solution indicated in general a fairly good separation of tantalum from niobium. Crotonaldehyde, which has the same formula as butyraldehyde except for a carbon to carbon double bond in the 2, 3 position, extracted more tantalum but of lower purity than butyraldehyde. In light of the data for the heptanones, it might be expected that butyraldehyde with a carbonyl group at the end of the molecule would yield a high mass transfer and a high tantalum-niobium separation factor. However, it extracted a relatively small amount of high purity tantalum. Commercial grade furfural yielded a tantalum-niobium separation factor and mass transfer which would work very efficiently in a large scale multistage extraction process.

The esters with the exception of n-butyl d-tartrate, ethyl acetoacetate and triethyl citrate extracted less than 12 per cent of the material from the 22 per cent stock solution. Benzyl acetate and ethyl salicylate failed to extract any detectable tantalum or niobium. Comparison of the data for tributyl, tripropyl and triethyl citrate indicated that the shorter the alkyl group the higher the mass transfer and separation factor. In general, most of the esters do not appear practical for separating niobium and tantalum on a large scale.

Only diethyl ether of the ether organic class that was tested

extracted appreciable quantities of material from the diluted stock solutions. Most of the ethers appear not to extract any niobium or tantalum although alcohols and ketones with a similar number of carbon atoms extract appreciable amounts. No reason is known for this somewhat anomalous behavior.

Of all the organic compounds tested the water-immiscible amines generally transferred the most material to the organic phase. It is assumed that the amine salts of the fluotantalic and fluoniobic acid are formed and extracted. Although the mass transfer was high, the separation factors were low. It is evident from the data that for the amines tested the highest tantalum-niobium separation factor was 15 while as much as 89 per cent of the material expressed as oxides was transferred to the organic phase. Although these amines do not appear practical for the separation of niobium from tantalum in hydrofluoric acid solution, they might be useful for purifying niobium-tantalum mixtures by extracting them completely into the organic phase and away from other impurities.

The organic phosphates and phosphites extracted appreciable quanities of niobium and tantalum from the dilute aqueous stock solution. A comparison of the data for the tri-2-ethyhexyl phosphate and phosphite indicates that the latter gives a much higher separation factor and a higher relative tantalum purity in the equilibrium organic phase. However, the phosphate compound extracts appreciably more tantalum. Tributyl phosphate gave a very favorable tantalum-niobium separation factor and a favorable mass distribution. In general, the organic phosphates and phosphites appear to be quite useful for separating tantalum from niobium from their aqueous hydrofluoric acid solution.

It is apparent from Table 2 that aromatic and aliphatic hydrocarbons as well as chlorinated hydrocarbons do not extract detectable amounts of niobium or tantalum from the diluted stock solution. Carbon disulfide, nitrobezene and isoamyl nitrite also appeared inert.

The extractions employing mixed organic solvents were carried out in an attempt to combine the favorable properties of the solvents. Since the low molecular weight ketones appeared effective for separating tantalum from niobium, a mixture of acetone and an immiscible low molecular weight ketone was employed for extraction. Unfortunately acetone acted like methyl ethyl ketone by increasing mass transfer to the organic phase while decreasing the tantalum-niobium separation factor and purity of the tantalum.

Since amines were known to increase mass distribution to the organic phase, Primene 81-T and Primene JM-T were added to various organic solvents. In all cases the transfer to the organic phase increased with addition of the Primenes while the tantalum-niobium separation factors and purity of tantalum decreased. The addition of the Primenes to heptane

or di-isobutyl ketone resulted in a considerable amount of transfer to the organic phase with some separation. It is believed that the presence of these amines would cause considerable extraction of tantalum and niobium from their hydrofluoric acid solution by many otherwise inert organic solvents with some separation of tantalum from niobium.

In the above discussion only the effects of organic solvents in extracting tantalum from niobium have been considered. Studies on variations of the aqueous hydrofluoric acid solutions indicated that its composition was very important in obtaining a successful separation process. The single stage data reported in Table 2 for extraction of the stock solution and its various water dilutions illustrate the effect of changing solute concentrations although their relative concentration values remain constant. For the single stage extractions reported in Table 3 the hydrofluoric acid concentration was kept constant while the total concentration of niobium and tantalum was varied. The single stage data in Table 4 indicate the effect of varying the hydrofluoric acid concentration at a constant concentration of niobium and tantalum.

Figure 2 shows the variation of mass transfer with per cent stock solution for extractions with methyl ethyl ketone, diethyl ketone and ethyl acetoacetate. For these organic solvents as well as all the others tested the per cent of material transferred to the organic phase decreased with per cent stock solution. The percentage of the total tantalum extracted by the organic phase showed a similar trend. It is apparent from Figure 2 that as the concentration of the stock solution decreased below 20 per cent the mass transfer to diethyl ketone decreased markedly.

From Figure 3 it can be noted that the material extracted by diethyl ketone contained higher purity tantalum as the per cent stock solution and mass transfer shown in Figure 2 decreased. These dilution effects were observed for all the organic liquids so tested. The greatest rate of change in percentage niobium oxide recovered from the organic phase occurred in the extraction of the 50 to 80 per cent stock solution. The tantalum which was extracted from the 5.0 per cent stock solution by diethyl ketone contained only 360 ppm niobium.

As the per cent stock solution decreased the tantalum-niobium separation factors increased. Figure 4, which shows this relationship, indicates that for an extremely dilute stock solution the separation factors would approach infinity. According to the laws of heterogeneous equilibrium when finite volumes of solutions containing finite amounts of niobium and tantalum are extracted, then there will be finite amounts of niobium and tantalum in both phases. The equilibrium organic phase could not become free of niobium by a practical extraction process. However, the niobium concentration might go below the limit of analytical detection, consequently, for practical purposes the product extracted by

Table 3

Single Stage Extractions of a 12.8 Molar HF Solution of Niobium and Tantalum with Diethyl Ketone

Initial Aq. Phase Gram pentoxide/ liter	Equil. anal. % Ta_2O_5 Aq.	Org.	K_{Ta}	K_{Nb}	Ta-Nb Sepn. factor	% total oxide weight in org.
41	17.0*	73.4	4.28	0.316	14	59.5
66	17.0	77.8	4.02	0.232	17	55.0
205	18.2	85.7	2.75	0.103	27	49.3
256	20.4	93.4	2.47	0.0448	55	47.8
310	19.3	95.5	2.17	0.0245	92	43.3
375	25.0	98.5	1.74	0.00885	197	40.6
506	26.0	99.5	1.63	0.00318	514	38.3

* Calculated value.

Table 4

Single Stage Extractions of a Niobium-Tantalum-Hydrofluoric Acid Solution Containing the Equivalent of 172 Grams of Oxide Per Liter with Diethyl Ketone

Initial Aq. Phase HF conc. (molar)	Equil. anal. % Ta_2O_5 Aq.	Org.	K_{Ta}	K_{Nb}	Ta-Nb Sepn. factor	% total oxide weight in org.
4.58	37.0	99.93	0.960	0.000390	2460	26.1
5.50	16.4	99.6	3.48	0.00271	1280	41.0
9.14	15.8	95.8	3.70	0.0302	123	46.0
12.8	18.2	86.5	2.98	0.105	28.4	48.6
14.7	23.5	82.9	2.40	0.153	15.7	53.4
20.2	48.4	62.5	1.12	0.593	1.89	60.4*
23.9	52.5	59.2	0.998	0.757	1.32	72.7*

*Additional weight probably caused by reaction of HF with containers.

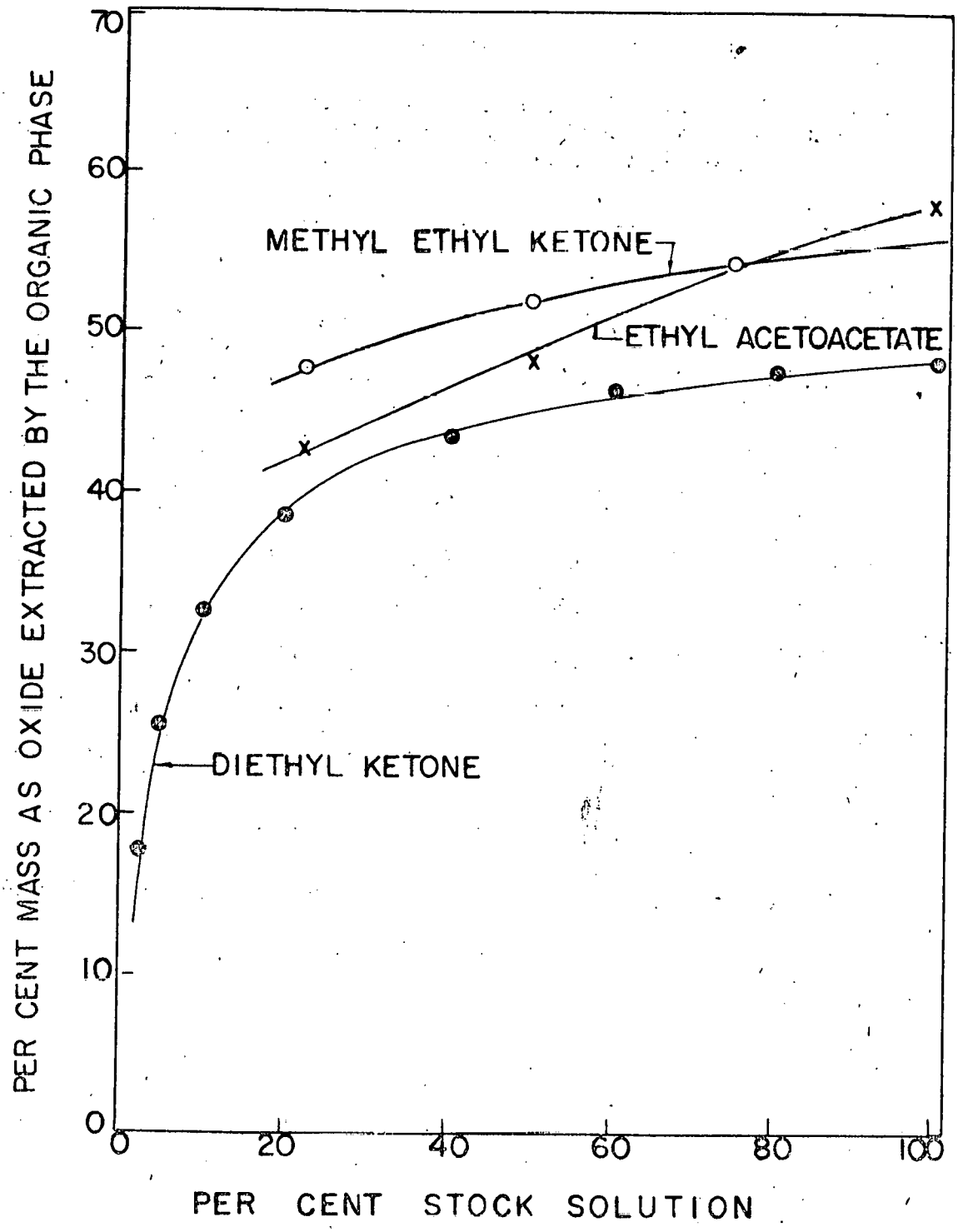

Figure 2 - Extraction of Niobium and Tantalum at Various Water Dilutions of the Stock Solution.

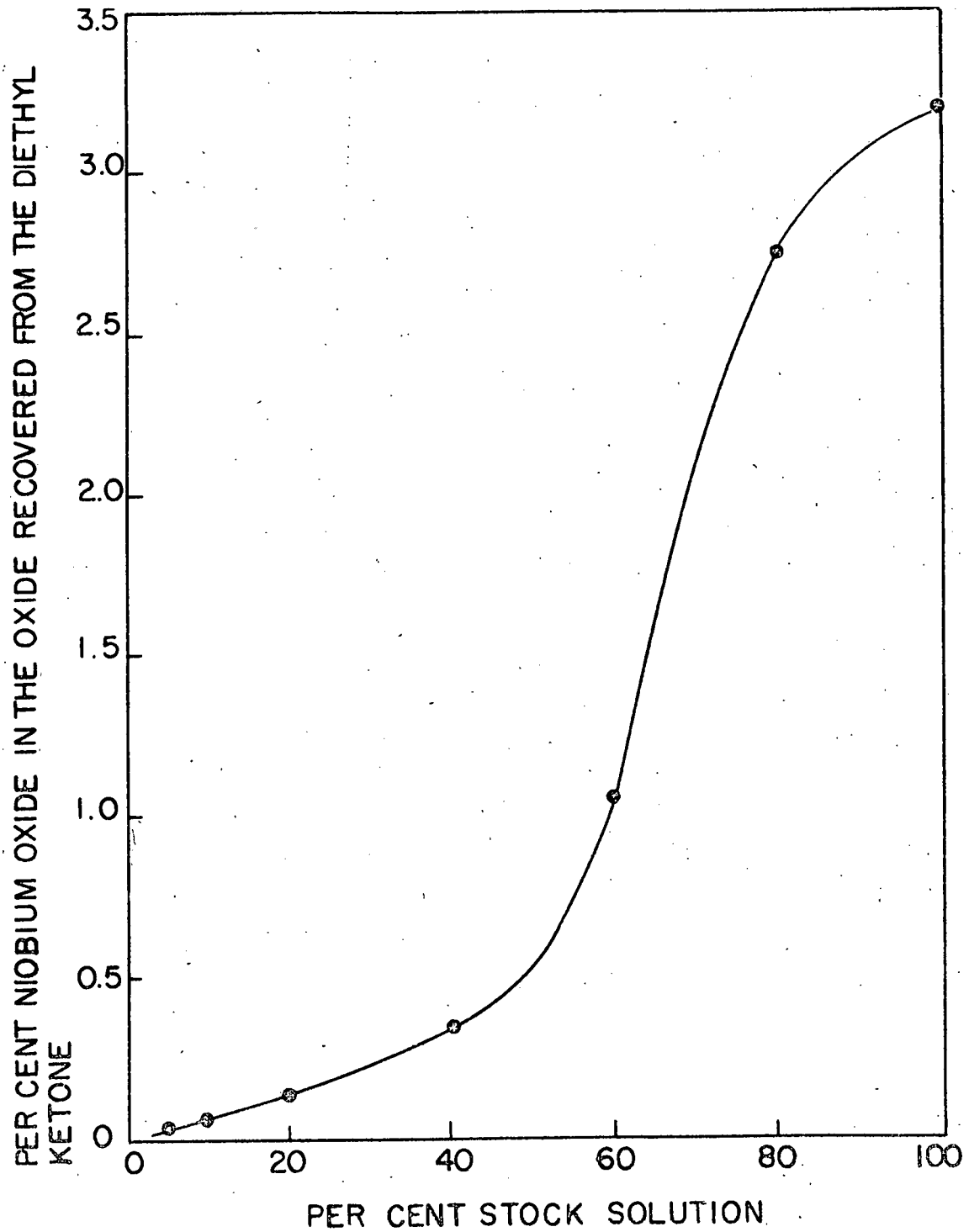

Figure 3 - Composition of the Product from Diethyl Ketone Extractions of Various Dilutions of the Stock Solution.

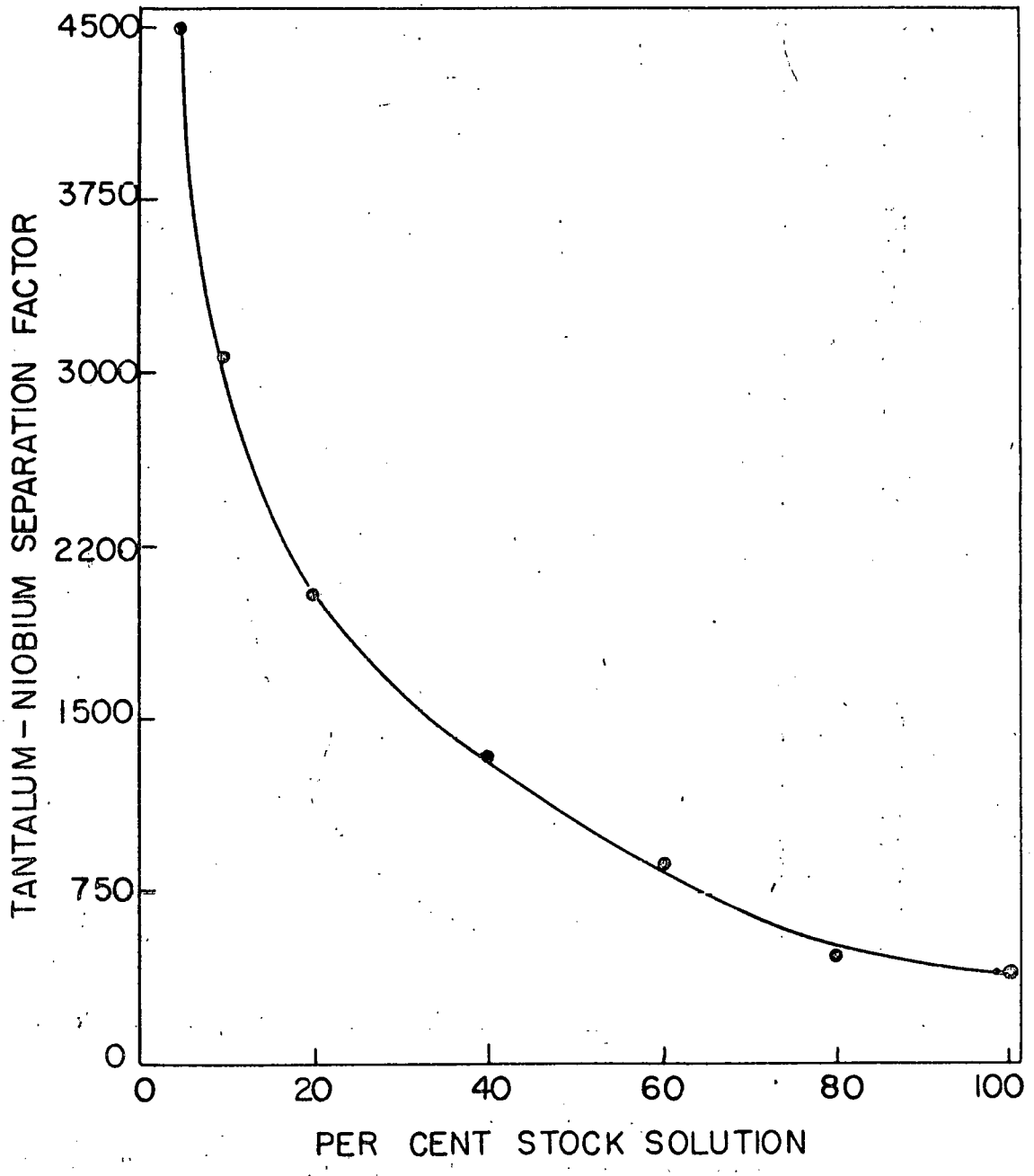

Figure 4 - Tantalum-Niobium Separation Factors for Extracting Various Dilutions of the Stock Solution with Diethyl Ketone.

the diethyl ketone organic phase could approach a purity considered to be free of niobium.

In Figure 5 it is shown that the variation in the tantalum-niobium separation factor with mass transfer for diethyl ketone is linear over the range studied. In light of the above data it is apparent that as the mass transfer approaches zero, or as dilution of the stock solution approaches infinity, the separation factor must become increasingly large. Consequently, this variation of separation factor with mass distribution, shown in Figure 5, might not remain linear over the range of low mass transfer not covered in the figure.

Another series of single stage extractions was carried out employing pure diethyl ketone as the organic phase. The aqueous phases were prepared by dissolving various amounts of the mixed hydrated oxides in 12.8 molar hydrofluoric acid. This hydrated oxide mixture was obtained by precipitating various volumes of the stock solution with ammonium hydroxide. The data for these extractions appear in Table 3.

This variation of mass transfer to the organic phase with concentration of niobium and tantalum in the initial aqueous phase is illustrated graphically in Figure 6 while the relationships between the equivalent oxide concentration in the aqueous and organic phases appear in Figure 7. It is apparent from the data of Table 3 and Figure 6 that an increase in the concentration of niobium and tantalum in the initial aqueous phase resulted in a decrease for per cent mass transfer to the organic phase. However, the material which was extracted by the organic phase increased in relative tantalum purity. It can be seen in Table 3 that the distribution coefficients for niobium and tantalum decreased with increasing oxide concentration. It is obvious that the concentration of free hydrofluoric acid in the system decreased as the amounts of niobium and tantalum increased. It appears from these data that the presence of excess free hydrofluoric acid reduces the effectiveness of the separation of tantalum from niobium although increasing their transfer to the organic phase.

This possibility was investigated further by carrying out a series of single stage extractions employing diethyl ketone as the organic phase and an aqueous phase containing 172 grams of combined niobium and tantalum oxides per liter at various hydrofluoric acid concentrations. The data from these extractions appear in Table 4.

These data show that the addition of hydrofluoric acid to the system at a constant niobium and tantalum concentration increases the mass transfer to the organic phase while decreasing the tantalum-niobium separation factor. The purity of the tantalum relative to niobium extracted by the organic phase also decreased. The distribution coefficient

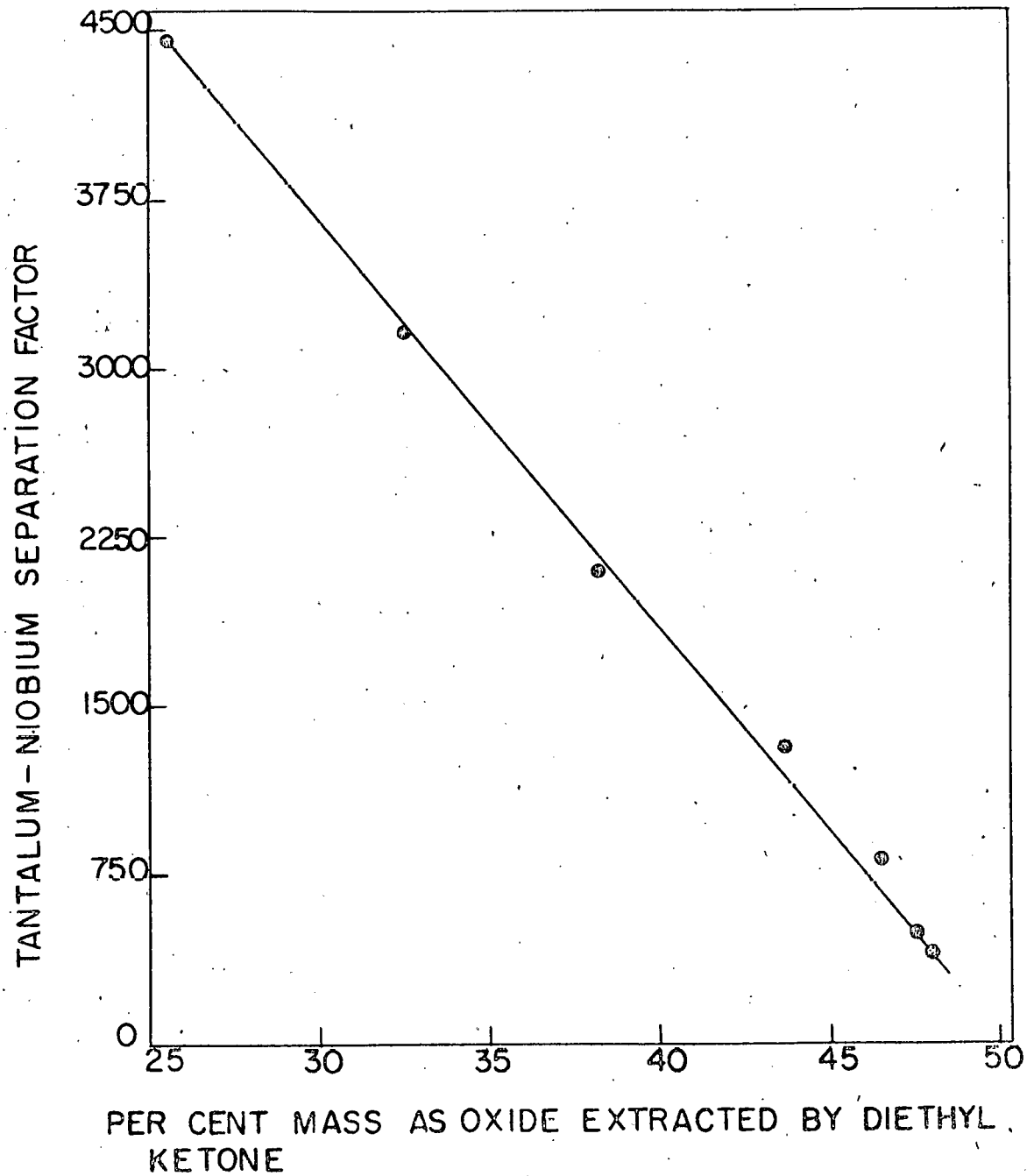

Figure 5 - Tantalum-Niobium Separation Factors at Various Mass Distribution Values.

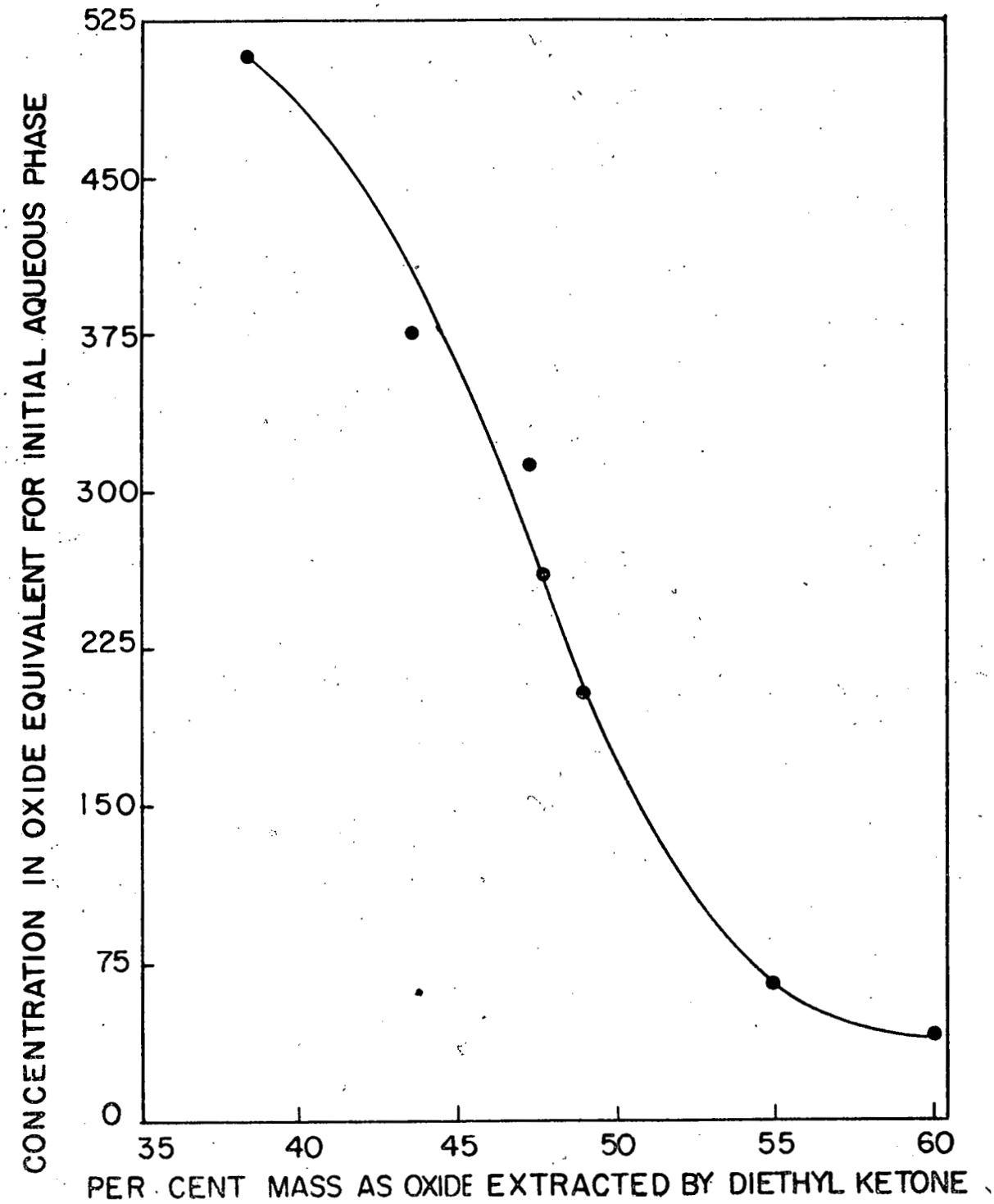

Figure 6 - Effect of Niobium and Tantalum Concentration on Mass Distribution at Constant Fluoride Concentration.

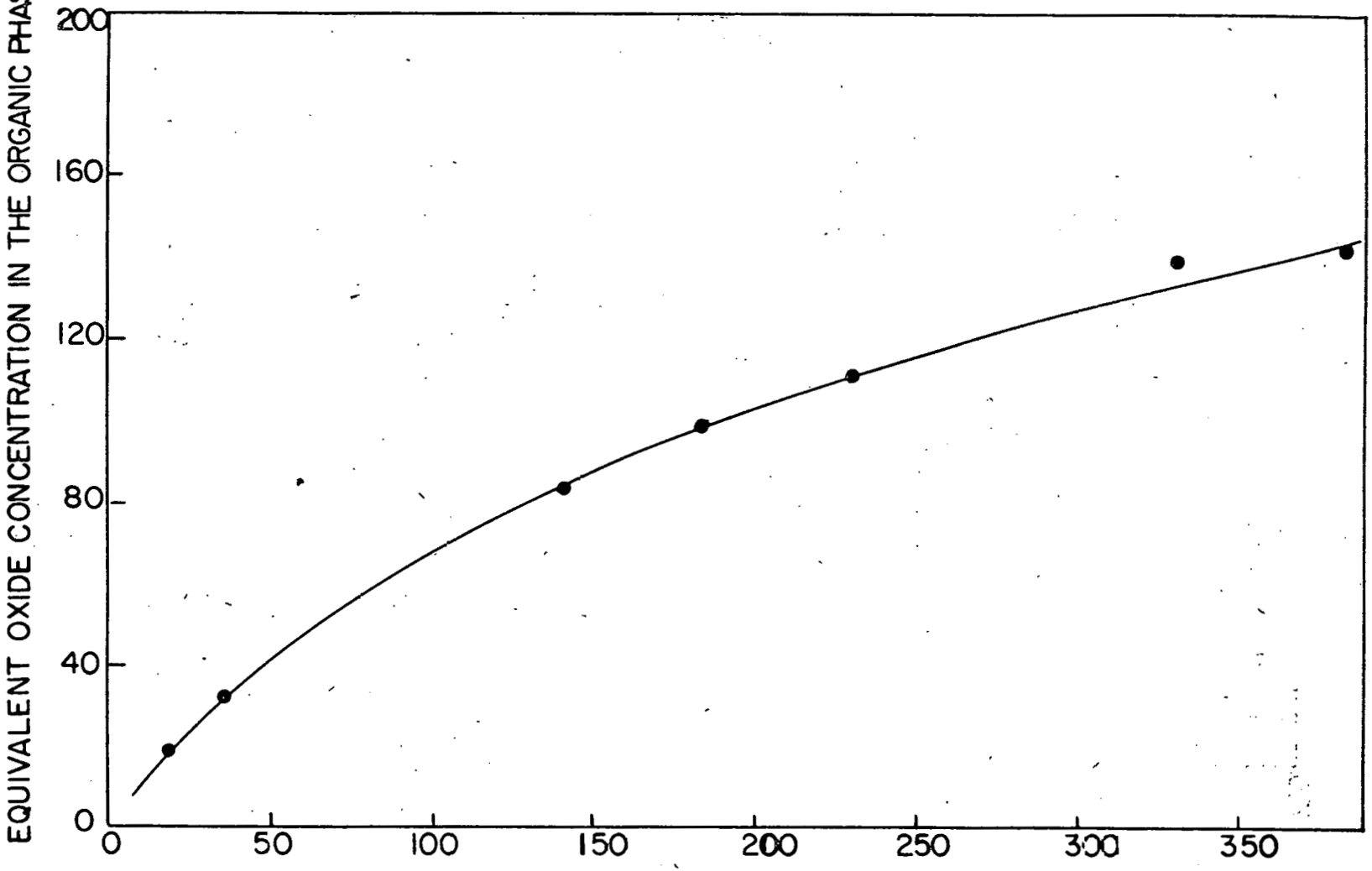

Figure 7 - Distribution of the Niobium-Tantalum Mixture between Aqueous Hydrofluoric Acid and Diethyl Ketone.

for niobium gradually increased with hydrofluoric acid concentration while the tantalum distribution values reached a maximum at about 9 molar hydrofluoric acid. This indicates that hydrofluoric acid increases the extractability of niobium by diethyl ketone while decreasing the extractability of tantalum over much of the acid range. This is indicated by the very rapid decrease in the tantalum-niobium separation factors for the addition of hydrofluoric acid. It can be noted in Table 4 that the separation factor was 2460 for the practically saturated solution of earth acids in hydrofluoric acid while for the 23.9 molar acid system the separation factor was only 1.32.

The data in Tables 2, 3 and 4 for the single stage extractions of the hydrofluoric acid solution of niobium and tantalum with diethyl ketone illustrate several important points. Dilution of the stock solution with water did not change the numerical value of the ratio of hydrofluoric acid concentration to niobium plus tantalum concentration. Extractions of these diluted aqueous stock solutions yielded very pure tantalum in the equilibrium organic phase. The data in Tables 3 and 4 indicate that when this ratio of acid concentration to the niobium plus tantalum concentration increased, the amount of material transferred to the organic phase increased while its tantalum purity decreased. When this ratio was decreased the opposite trends were observed. It appears, therefore, that the concentration of tantalum, niobium and hydrofluoric acid as well as their ratios are important in determining the purity and amount of tantalum extracted by the organic phase.

For highly preferential extraction of tantalum from niobium when they are together in hydrofluoric acid solution, it appears that the ratio of acid concentration to the niobium and tantalum concentrations should be as low as possible. This means that the earth acids should be dissolved in a minimum amount of hydrofluoric acid. However, if a large excess of hydrofluoric acid is present, a dilution of the aqueous solution with water permits a highly preferential extraction of tantalum from niobium. It is apparent that the amount of hydrofluoric acid, niobium, tantalum and water dilution is determined by the desired purity and recovery of tantalum.

A possible explanation for the lack of preferential extraction of tantalum at high hydrofluoric acid concentrations results from consideration of the probable niobium and tantalum species in this acid aqueous medium. It has been reported that fluotantalates, $TaF_7^=$, and pentafluoniobiates, $NbOF_5^=$, crystallize from a supersaturated fluoride solution. Consequently, for nearly saturated solutions of niobium and tantalum it appears reasonable to assume that these species are present in the aqueous phase. The formation of these species by the reaction of hydrofluoric acid with the earth acids probably results according to the overall reactions 1 and 2. However, in the presence of excess hydrofluoric acid it is possible that the product from reaction 2 might tend to undergo a further reaction 3. These reactions are:

$$7\ HF + H_3\ TaO_4 \rightleftharpoons H_2\ TaF_7 + 4\ H_2O \quad \text{Reaction 1}$$

$$5\ HF + H_3\ NbO_4 \rightleftharpoons H_2\ NbOF_5 + 3\ H_2O \quad \text{Reaction 2}$$

$$2\ HF + H_2\ NbOF_5 \rightleftharpoons H_2\ NbF_7 + H_2O \quad \text{Reaction 3}$$

It is apparent that the products of reactions 1 and 3 are very similar while the niobium and tantalum salts from reactions 1 and 2 are quite different. It would be expected that the relative extractability of the fluotantalates and the fluoniobiates might be similar while for the fluotantalates and the pentafluoniobiates it might be different. If this assumption is correct, an amount of hydrofluoric acid insufficient to yield appreciable amounts of reactions 3 should result in a considerable relative difference in niobium and tantalum extractability. Although this approach is very qualitative, it does offer an explanation of the high tantalum-niobium separation factors at low hydrofluoric acid concentrations and low separation factors at high acid concentrations.

Extraction of the amine neutralized stock solution or its water dilutions.

A great number of common water-immiscible organic liquids separate tantalum from niobium when these elements are together in a hydrofluoric acid solution. However, this system because of its corrosive nature toward glass and most metals cannot be employed in ordinary equipment for continuous separation work. Therefore, other effective liquid-liquid systems for the separation of niobium from tantalum were developed in an effort to obtain conditions of extractions that would permit prolonged use of glass equipment.

Before these extraction separation studies could be considered, an essentially non-corrosive aqueous solution of niobium and tantalum was required. Consequently, various organic amines were added to the 22 per cent stock solution of niobium and tantalum to neutralize the free hydrofluoric acid by forming the amine salt. A great variety of results were obtained. Additions of dibutyl amine, tributyl amine, tertiaryoctyl amine, phenylhydrazine, aminohydroquinone dimethyl ether or aminohydroquinone diethyl ether caused immediate precipitation. When aniline, m-toluidine or o-toluidine was added to the aqueous phase, a second liquid phase appeared at a pH of from 4 to 6 although no precipitation was immediately evident. A partially neutralized aqueous solution containing any one of these three amines was not stable for more than two hours before a precipitate would start to form. However, neutralization by

o-tolyl propanolamine to a pH of about 5 gave an aqueous phase which contained only a small amount of precipitate after standing for 24 hours.

Solutions that were indefinitely stable were obtained by adding monoethanolamine, diethanolamine, triethanolamine, 3-aminopropanol, aminoethyl ethanolamine or diethyl ethanolamine to this hydrofluoric acid solution of niobium and tantalum. For the first aliphatic hydroxyamine of this series a pH of 7.5 was reached before precipitation occurred while the addition of large excess amounts of all the other compounds gave no precipitate. Phenyl ethyl ethanolamine, phenyl diethanolamine and m-tolyl diethanolamine formed a second liquid phase at a pH of from 4 to 6 when added to the 22 per cent stock solution of niobium and tantalum. This partially neutralized aqueous solution was indefinitely stable. Repetition of these experiments while employing the 100 per cent stock solution of niobium and tantalum gave the same results. The hydroxyamines were the only class of organic amines which neutralized the hydrofluoric acid mixture of niobium and tantalum to give an indefinitely stable solution. An assumption is that the amino group reacts with the free hydrofluoric acid to neutralize the solution while the hydroxy group reacts with the fluoacids of niobium and tantalum to form a soluble complex. All pH values were determined by employing universal pH paper.

The corrosion of these amine-hydrofluoric acid solutions of niobium and tantalum on Pyrex glass was tested. Glass rings after being submerged in the various solutions for definite time increments were removed, cleaned, dried and weighed. Figure 8 shows the loss of weight of the glass per square inch of surface as a function of time submerged for the aqueous solutions having various pH values. The pH values were obtained by neutralizing the 22 per cent stock solution with different amounts of phenyl ethyl ethanolamine. It is apparent from Figure 8 that for pH values of 4 or above little variation in the weight loss of the Pyrex glass with time resulted. This is illustrated in Figure 9 where the average rate of weight loss during the first 50 hours of contact time is plotted as a function of pH. This indicates clearly that the amine-hydrofluoric acid solutions having a pH of from 4 to 6 react slowly with Pyrex glass. Experiments using several other amines in place of phenyl ethyl ethanolamine for neutralizing the stock solution and its water dilutions indicated about these same rates of corrosion at the similar pH value.

The corrosion rate of 0.045 milligrams per square inch per hour which results at a pH of from about 4 to 6 represents a decrease of 33 times from the corrosion rate of the pure 22 per cent stock solution. Since these rates of corrosion were obtained for a stationary solution, somewhat larger values could be expected in the presence of flowing liquids. However, these corrosion data indicate the possibility of prolonged use of the laboratory glass equipment to extract the amine-

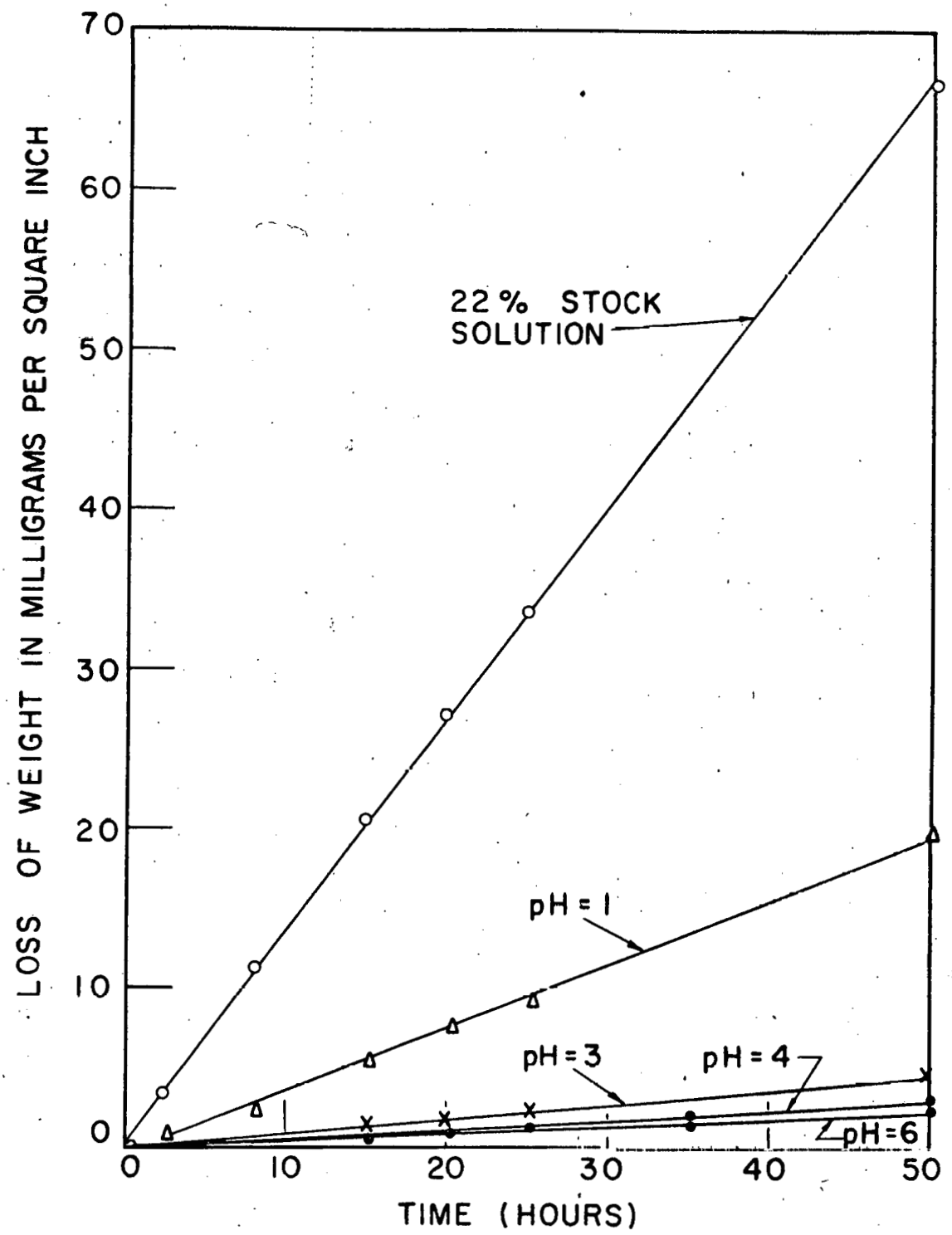

Figure 8 - Loss in Weight of Pyrex Glass Submerged in Amine Neutralized Hydrofluoric Acid Solutions of Niobium and Tantalum.

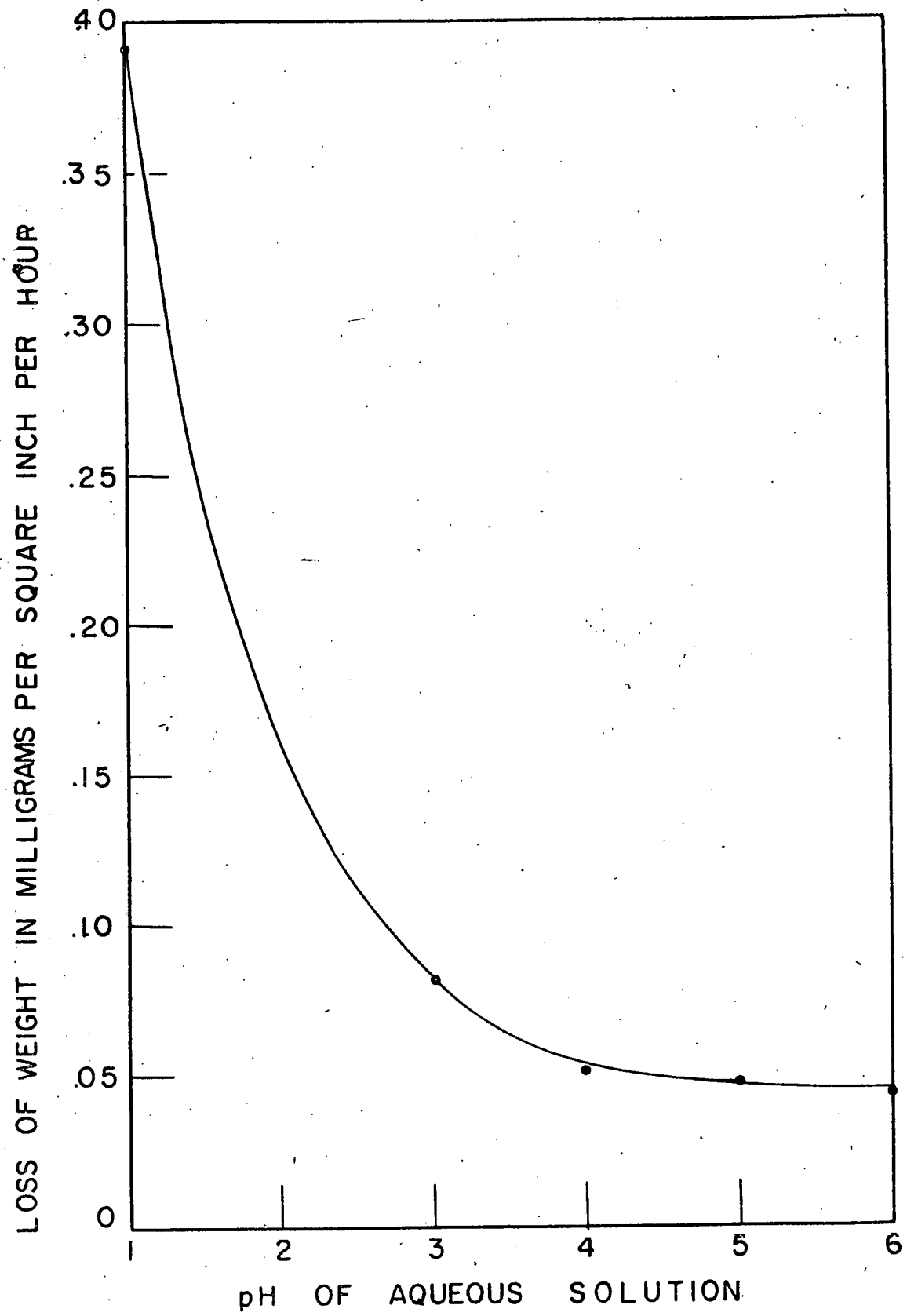

Figure 9 - Rate of Corrosion as a Function of pH.

hydrofluoric acid solution of niobium and tantalum.

Although some of these amine-hydrofluoric acid salt solutions of niobium and tantalum attack glass slowly, they would be of little value in separation unless an organic solvent could be found which preferentially extracts niobium or tantalum. Consequently, a large number of single stage extractions of various partially neutralized amine-hydrofluoric acid solutions of niobium and tantalum were carried out. Unless otherwise indicated, the relative volumes for these single stage extractions were two volumes of the organic liquid to one volume of the aqueous liquid. Glass equipment was used to carry out these experiments.

Table 5 contains the numbers and compositions of the various aqueous amine-hydrofluoric acid solutions of niobium and tantalum employed in this study. These aqueous phases were prepared by adding the amine to either the stock solution or its 22 per cent water solution. The amount of amine added, as shown in Table 5, is based on 10.0 milliliters of the original amine-free hydrofluoric acid solution of niobium and tantalum. When the amount of amine which was added to the aqueous solution was sufficient to form a second phase, the resulting amine feed solution was considered to be saturated with the amine.

The data for the single stage extraction of these amine-salt feed solutions are given in Table 6. The extractions are divided into groups according to the aqueous amine feed solution employed. These groups are subdivided alphabetically according to organic phase employed. When the weight of oxide obtained from one of the product phases was very small, either product was analyzed.

It is apparent from the single stage extraction in Table 6 that a preferential extractability of tantalum resulted for all of these amine-hydrofluoric acid salt solutions of niobium and tantalum. The degree of extractability and the tantalum-niobium separation factors were a function of the nature and amount of amine employed to neutralize the hydrofluoric acid solution. In all cases the tantalum-niobium separation factors obtained from extracting these amine feed solutions were considerably lower than those obtained from extracting the corresponding amine-free hydrofluoric acid solutions of niobium and tantalum with the same organic compound. However, in many extractions the corresponding mass transfer to the organic phase was considerably higher for the amine feed solutions.

Many extractions of amine feed solution 1 are not listed in Table 6 because they resulted in less than 10 per cent transfer of the material to the organic phase. Two volumes of the organic phase to one volume of aqueous phase were employed for each of these unlisted extractions. The unlisted organic solvents which did not extract more than 10 per cent of the niobium and tantalum from amine feed solution 1 were: amyl alcohol (tertiary), aniline, butanol (n), dibutyl amine, ethyl aceto-

Table 5

Neutralization of 10.0 Milliliters of the HF Solution of Niobium and Tantalum with Amines

Amine feed soln.	Amine	% stock soln.	Amount of amine added	pH	Grams oxide/ liter
1	Diethanolamine	22	1.8 ml.	5	101
2	Diethanolamine	22	3.6 ml.	7	90
3	Diethanolamine	22	5.4 ml.	9	80
4	Monoethanolamine	22	1.1 ml.	5	104
5	Triethanolamine	22	2.0 ml.	5	95
6	Diethyl ethanolamine	22	2.3 ml.	5	93
7	Aminoethyl ethanolamine	22	1.0 ml.	5	103
8	3-Aminopropanol	22	1.2 ml.	5	106
9	Aniline	22	1.0 ml.	5(sat'd)	106
10	50 Vol. % analine + 50 vol. % mono-ethanolamine	22	1.0 ml.	5(sat'd)	105
11	Phenyl ethyl ethanolamine	22	2.1 ml.	5(sat'd)	95
12	Phenyl ethyl ethanolamine	100	10.0 ml.	5(sat'd)	260
13	m-Tolyl diethanol-amine	22	2.3 g.	4(sat'd)	95
14	Phenyl diethanol-amine	22	2.3 g.	4(sat'd)	97
15	Phenyl diethanol-amine	100	11.0 g.	4(sat'd)	262

Table 6

Single Stage Extractions of the Amine-Hydrofluoric Acid Solutions of Niobium and Tantalum

Ext. no.	Aq. phase amine feed soln.	Organic phase (vol. %)	Equil. anal. % Ta_2O_5 Aq.	Org.	K_{Ta}	K_{Nb}	Ta-Nb sepn. factor	% total oxide weight in org.
1	1	Diethyl ketone	----	I.S.	----	----	----	1.0
2	1	5% tert-octylamine + 95% diethyl ketone	43.4	69.7	0.631	0.207	3.0	43.4
3	1	Primene 81-T	I.S.	----	----	----	----	99.8
4	1	50% Primene 81-T + 50% diethyl ketone	I.S.	----	----	----	----	99.4
5	1	25% Primene 81-T + 25% diethyl ketone	I.S.	----	----	----	----	98.2
6	1	12.5% Primene 81-T + 87.5% diethyl ketone	6.40	60.0	38.9	1.77	21.9	90.0
7	1	6.3% Primene 81-T + 93.7% diethyl ketone	17.6	74.1	3.41	0.255	13.4	63.9
8	1	5.0% Primene 81-T + 95.0% diethyl ketone	20.4	82.9	2.16	0.114	19.0	53.9

I.S. = Insufficient sample.

Table 6 (Continued)

Ext. no.	Aq. phase: amine feed soln.	Organic phase (vol. %)	Equil. anal. % Ta_2O_5 Aq.	Equil. anal. % Ta_2O_5 Org.	K_{Ta}	K_{Nb}	Ta-Nb sepn. factor	% total oxide weight in org.
9	1	3.2% Primene 81-T + 96.9% diethyl ketone	33.1	88.0	0.0799	0.0537	14.8	39.1
10	1	5.0% Primene 81-T + 95% fuel oil	35.3	74.8	0.907	0.168	5.45	49.0
11	1	5.0% Primene 81-T + 95% heptane	35.3	74.5	0.910	0.171	5.33	48.0
12	1	5.0% Primene 81-T + 95% kerosene	35.7	75.8	0.945	0.167	5.65	49.6
13	1	5.0% Primene 81-T + 95% toluene	32.8	74.8	1.10	0.181	6.12	51.8
14	1	5.0% Primene 81-T + 95% turpentine	39.7	77.8	0.602	0.113	5.32	40.6
15	1	50% Primene JM-T + 50% diethyl ketone			Slurry formation			
16	1	25% Primene JM-T + 75% diethyl ketone	28.6	59.2	5.28	1.46	3.62	85.7
17	1	12.5% Primene JM-T + 87.5% diethyl ketone	25.9	69.7	2.21	0.337	6.56	65.4
18	1	5.0% Primene JM-T + 95% diethyl ketone	42.9	87.2	0.598	0.0644	9.30	36.1

Table 6 (Continued)

Ext. no.	Aq. phase: amine feed soln.	Organic phase (vol. %)	Equil. anal. % Ta_2O_5 Aq.	Equil. anal. % Ta_2O_5 Org.	K_{Ta}	K_{Nb}	Ta-Nb sepn. factor	% total oxide weight in org.
19	1	m-Toluidine	38.5	92.5	0.457	0.0230	19.8	32.1
20	2	Diethyl ketone	----	I.S.	----	----	----	0.33
21	2	25% tert-octylamine + 75% diethyl ketone	52.6	58.5	0.685	0.545	1.26	48.2
22	2	12.5% tert-octylamine + 87.5% diethyl ketone	52.6	57.8	0.346	0.281	1.23	33.5
23	2	50% Primene 81-T + 50% diethyl ketone	51.6	57.7	2.35	1.84	1.28	82.3
24	2	25% Primene 81-T + 75% diethyl ketone	53.5	60.0	0.677	0.512	1.31	56.2
25	2	12.5% Primene 81-T + 87.5% diethyl ketone	52.6	57.8	0.298	0.248	1.21	36.2
26	2	6.3% Primene 81-T + 93.7% diethyl ketone	53.4	61.9	0.151	0.107	1.41	21.4
27	2	5.0% Primene 81-T + 95% diethyl ketone	53.5	61.9	0.123	0.0870	1.41	18.0
28	2	3.1% Primene 81-T + 96.9% diethyl ketone	----	I.S.	----	----	----	11.8

Table 6 (Continued)

Ext. no.	Aq. phase amine feed soln.	Organic phase (vol. %)	Equil. anal. % Ta_2O_5 Aq.	Org.	K_{Ta}	K_{Nb}	Ta-Nb sepn. factor	% total oxide weight in org.
29	3	25% tert-octylamine + 75% diethyl ketone	----	I.S.	----	----	----	2.05
30	3	Primene 81-T	52.5	57.7	0.0642	0.0542	1.19	10.9
31	3	25% Primene 81-T + 75% diethyl ketone	----	I.S.	----	----	----	2.85
32	3	12.5% Primene 81-T + 87.5% diethyl ketone	----	I.S.	----	----	----	1.90
33	3	5% Primene 81-T + 95% diethyl ketone	----	I.S.	----	----	----	0.72
34	4	12.5% Primene 81-T + 87.5% diethyl ketone	9.94	60.5	29.6	2.12	14.0	92.3
35	4	5.0% Primene 81-T + 95% diethyl ketone	33.1	73.6	1.17	0.208	5.62	55.0
36	5	5.0% Primene 81-T + 95% diethyl ketone	31.6	75.5	1.59	0.238	6.68	59.2
37	6	5.0% Primene 81-T + 95% diethyl ketone	29.0	76.5	1.57	0.197	7.97	57.8
38	7	5.0% Primene 81-T + 95% diethyl ketone	42.9	68.1	1.07	0.381	2.82	53.4

Table 6 (Continued)

Ext. no.	Aq. phase: amine feed soln.	Organic phase (vol. %)	Equil. anal.: % Ta_2O_5 Aq.	Equil. anal.: % Ta_2O_5 Org.	K_{Ta}	K_{Nb}	Ta-Nb sepn. factor	% total oxide weight in org.
39	8	12.5% Primene 81-T + 87.5% diethyl ketone	7.72	60.5	37.2	2.03	18.3	91.7
40	8	5.0% Primene 81-T + 95% diethyl ketone	25.4	80.2	1.69	0.143	11.8	53.0
41	9	5.0% Primene 81-T + 95% diethyl ketone	1.60	83.9	34.1	0.106	321	60.8
42	10	5.0% Primene 81-T + 95% diethyl ketone	7.49	94.2	6.68	0.0334	200	55.6
43	10	5.0% Primene 81-T + 95% heptane	17.0	88.4	2.51	0.0672	37.3	51.2
44	11	Diethyl ketone	22.0	99.3	1.24	0.00245	506	38.8
45	11	5.0% Primene 81-T + 95% diethyl ketone	1.51	80.4	38.3	0.143	268	63.9
46	12	Cyclohexanone	18.1	81.0	4.51	0.234	19.3	59.0
47	12	Diethyl ketone*	40.5	96.7	0.652	0.0150	43.3	26.5
48	12	Diethyl ketone	32.7	98.4	0.566	0.00443	128	34.0

*Equal volumes of the organic and aqueous phases were employed.

Table 6 (Continued)

Ext. no.	Aq. phase amine feed soln.	Organic phase (vol. %)	Equil. anal. % Ta_2O_5 Aq.	Equil. anal. % Ta_2O_5 Org.	K_{Ta}	K_{Nb}	Ta-Nb sepn. factor	% total oxide weight in org.
49	12	Heptane	----	----	----	----	----	0
50	12	Isophorone*	27.3	94.5	1.38	0.0312	44.3	40.2
51	12	Isophorone	21.4	94.7	3.68	0.0559	65.8	46.8
52	12	Mesityl oxide*	37.4	94.5	0.850	0.0270	31.5	32.1
53	12	Mesityl oxide	25.0	96.2	3.00	0.0392	76.5	40.2
54	12	Methyl isobutyl ketone*	44.8	98.3	0.523	0.00735	71.3	23.6
55	12	Methyl isobutyl ketone	37.5	98.0	0.380	0.00477	79.8	27.9
56	12	Tributyl phosphate*	31.1	95.6	1.22	0.0256	47.8	41.2
57	12	Tributyl phosphate	17.4	92.8	1.34	0.0220	61.0	49.1
58	13	Diethyl ketone	20.4	98.9	1.43	0.00399	358	40.6
59	14	Cyclohexanone	14.6	94.6	2.12	0.0207	103	47.4
60	14	Diethyl ketone	30.8	99.7	0.690	0.00105	657	35.0
61	14	Ethyl acetoacetate	21.7	96.7	1.30	0.0124	105	41.7
62	14	Isophorone	18.7	98.1	1.39	0.00635	219	43.2

Table 6 (Continued)

Ext. no.	Aq. phase: amine feed soln.	Organic phase (vol. %)	Equil. anal. % Ta_2O_5: Aq.	Equil. anal. % Ta_2O_5: Org.	K_{Ta}	K_{Nb}	Ta-Nb sepn. factor	% total oxide weight in org.
63	14	Mesityl oxide	21.7	98.8	1.18	0.00413	286	38.9
64	14	Methyl isobutyl ketone	37.4	99.5	0.515	0.00183	281	30.8
65	15	Amyl alcohol (n)	49.7	88.0	0.163	0.0219	7.45	7.80
66	15	Cyclohexanone	8.95	76.5	3.20	0.0964	33.1	68.6
67	15	Diethyl ketone	28.2	98.4	0.675	0.00444	152	36.4
68	15	Ethyl acetoacetate	23.0	88.5	1.08	0.0420	25.7	49.1
69	15	Heptanol-3	47.3	95.3	0.0832	0.00375	22.3	9.75
70	15	Isophorone	13.0	93.6	1.92	0.0196	97.8	52.5
71	15	Mesityl oxide	20.9	96.2	1.01	0.0104	97.2	43.7
72	15	Methyl ethyl ketone	16.4	72.9	1.83	0.134	13.6	71.3
73	15	Methyl n-hexyl carbinol	48.4	96.9	0.0710	0.00212	33.4	7.94
74	15	Methyl isobutyl ketone	40.0	98.8	0.319	0.00251	12.7	26.7
75	15	Tributyl phosphate	18.2	94.1	1.19	0.0168	70.8	48.8

acetate, isophorone, mesityl oxide, methyl ethyl ketone, 2,4-pentanedione, o-tolyl propanolamine, tributyl amine and tributyl phosphate. It is evident from these data that only certain organics extracted appreciable material from amine feed solution 1. About one-third of the total initial material was extracted by m-toludine. The product from this organic phase analyzed about 93 per cent tantalum oxide. Primene 81-T on the other hand extracted essentially all the niobium and tantalum from amine feed solution 1 although about one hour was required for phase separation.

Since diethyl ketone did not extract much tantalum and niobium from amine feed solution 1, it was used as an inert solvent for diluting Primene 81-T. It is apparent from extractions 3 to 9 inclusive in Table 6 that decreasing the amount of Primene 81-T also decreased the mass distribution to the organic phase. However, as little as 3.2 volume per cent Primene 81-T in diethyl ketone extracted about 40 per cent of the material in terms of oxide. The tantalum-niobium separation factors which resulted from the extractions of amine feed solution 1 with a solution of Primene 81-T in diethyl ketone ranged in value from 13 to 22 with no apparent definite trend. However, the purity of the tantalum oxide obtained from the organic extraction solutions rapidly increased as the amount of Primeme 81-T decreased (or as pure diethyl ketone was approached).

Similar extractions were carried out employing a solution of Primene JM-T (extractions 15 to 18 inclusive) or tertiaryoctylamine (extraction 2) in diethyl ketone as the organic phase. The same general trends as reported above, resulted although under similar extraction conditions Primene JM-T yielded lower tantalum-niobium separation factors and mass transfer than Primene 81-T. Tertiaryoctylamine, which is similar in structure but has a lower molecular weight than either Primene 81-T or Primene JM-T, resulted in lower separation factors than these Primene compounds under similar conditions of extraction. However, its corresponding mass transfer was greater than obtained for the Primene JM-T system although less than for the Primere 81-T system. It is apparent, therefore, that for similar conditions of extraction Primene 81-T yields a greater tantalum-niobium separation factor and mass transfer to the organic phase than either of these other two tertiary alkyl amines.

Since diethyl ketone is a relatively expensive diluent for Primene 81-T (about 75 cents per pound in 55 gallon drum lots), several cheaper water-immiscible organic liquids were substituted in its place. The data obtained by extracting amine feed solution 1 with these systems (extractions 10 to 14, inclusive) indicated that the use of fuel oil, heptane, kerosene, toluene or turpentine in place of diethyl ketone generally decreased only slightly the mass transfer to the organic phase. However, the tantalum-niobium separation factors resulting from the use of these cheaper organic solvents had a value of approximately 5.5 as compared to 19 for diethyl ketone. Perhaps the ketone forms a complex with

Primene 81-T making it more selective for extracting tantalum while the hydrocarbon solvents are incapable of forming such a complex. It is apparent, however, that the material for diluting Primene 81-T is also an important factor in separating tantalum from niobium when they are together in an amine-hydrofluoric acid salt solution.

Comparison of the data for extracting amine solutions 1, 2 and 3 illustrate the effect of pH, or the amount of diethanolamine present, on mass transfer and niobium and tantalum separation. In each case where the organic phase was the same, the per cent material tranferred to the organic phase decreased as the pH of the initial aqueous phase increased. For extraction of amine feed solution 3 the amount of transfer to the organic phase was generally too small to obtain a niobium and tantalum analysis. The tantalum-niobium separation factors also decreased with increasing pH of the initial aqueous phase. The separation factors obtained by extracting amine feed solutions 2 and 3, where the pH values were 7 and 9, respectively, were never greater than 1.4. However, tantalum was still preferentially extracted by the organic phase. These data indicate that addition of excess diethanolamine decreases considerably the extractability and effective separation of tantalum from niobium. Evidently the pH of the amine solution must be kept quite acidic if mixtures of niobium and tantalum are to be separated in relatively few stages.

The data for the extraction of the amine feed solutions 1, 4, 5, 6, 7 and 8 of Table 5 with a solution of Primene 81-T in diethyl ketone illustrate the relative effects of the presence of several aliphatic hydroxyamines. It is assumed that in preparing each of these amine feed solutions essentially the same number of equivalents of the amino group was added per unit volume of the 22 per cent stock solution. Since the pH value of 5 was determined by employing universal pH paper, small deviations resulted. Based on density values and the molecular weight of the aliphatic hydroxyamines, it was calculated that on an average 0.0187 equivalent of the amino group was required to neutralize 10.0 milliliters of the 22 per cent stock solution to a pH of 5.

Comparison of the results for the extraction of these aliphatic hydroxyamine feed solutions indicated similar mass distribution but varying tantalum-niobium separation factors. For the extraction with a 5.0 per cent solution of Primene 81-T in diethyl ketone, the mass transfer to the organic phase calculated as oxide varied from 53 to 59 per cent. However, the tantalum-niobium separation factor ranged from a value of 2.8 for amine feed solution 7 to a value of 19 for feed solution 1. The separation factors obtained for extraction of all the other aliphatic hydroxyamine solutions varied from 6 to 12. No explanation can be given for these variations in the tantalum-niobium separation factor. However, it is apparent that the choice of the aliphatic

hydroxyamines for neutralizing the hydrofluoric acid solution of niobium and tantalum does effect their separation.

Since these aliphatic hydroxyamines yielded relatively low tantalum-niobium separation factors, other systems non-corrosive to glass were investigated. The aniline neutralized solution, or amine feed solution 9, was stable for only 30 minutes. However, when it was extracted with a 5.0 per cent solution of Primene 81-T in diethyl ketone, as is indicated by extraction 52 of Table 6, a mass transfer of about 61 per cent and a tantalum-niobium separation factor of 321 resulted. Evidently the presence of an amine such as aniline is much more effective than the aliphatic hydroxyamines for separating tantalum and niobium. However, these aniline-neutralized hydrofluoric acid solutions of tantalum and niobium, because of their instability, would probably have to be processed soon after their preparation.

It was reported above that the aliphatic hydroxyamine feed solutions were indefinitely stable but upon extraction yielded low tantalum-niobium separation factors. On the other hand, the aniline-neutralized feed solution gave the opposite results. Consequently, a series of stability tests were carried out on the 22 per cent stock solution. After additions of various mixtures by volume of aniline and monoethanolamine to this hydrofluoric acid solution of tantalum and niobium until a pH of 5 was reached, the time required for a precipitate to form was observed. Precipitation started in about one hour for the 80 per cent aniline and 20 per cent monoethanolamine mixture while about 48 hours were required for precipitation from their 50-50 mixture. After 12 days all the samples which were neutralized with the mixture containing more than 30 per cent aniline had considerable amounts of precipitate present.

Since 48 hours was selected as an acceptable stability time, the amine feed solution 10 was prepared by neutralizing the 22 per cent stock solution to a pH of 5 with a 50-50 volume per cent mixture of aniline and monoethanolamine. As indicated by extractions 42 and 43 of Table 6, this feed solution was extracted with a 5.0 per cent solution of Primene 81-T in both diethyl ketone and heptane. In the former extraction, the resulting mass transfer of 55.6 per cent and tantalum-niobium separation factor of 200 were about intermediate in value to those obtained for extracting the corresponding feed solutions which had been neutralized with pure aniline or pure monoethanolamine. The use of heptane as a diluent for Primene 81-T decreased the separation factor considerably and the mass transfer percentage slightly. It is apparent from these data that the proper combination of monoethanolamine, aniline, Primene 81-T and diethyl ketone affords an effective system for separating tantalum and niobium from their hydrofluoric acid solution.

It is evident from the above data that extraction of an aqueous

phase containing both aniline and an aliphatic hydroxyamine gave not only a relatively stable solution but also a favorable separation of tantalum from niobium. Consequently, a series of extractions was carried out on a feed solution which consisted of a hydrofluoric acid solution of tantalum and niobium which had been partially neutralized with a derivative of aniline containing a hydroxy group. As is apparent from Table 5 these amines were phenyl ethyl ethanolamine, phenyl diethanolamine and m-tolyl diethanolamine. The amine feed solutions 11 to 15, inclusive, which contained these aromatic hydroxyamines, were indefinitely stable.

From the data for these extractions certain generalities are evident. Generally, extraction of these aniline derivative feed solutions resulted in smaller tantalum-niobium separation factors and mass transfer to the organic phase than was reported above for extraction of the corresponding hydrofluoric acid solution. The separation of tantalum from niobium was much more effective when extracting these aromatic hydroxyamines feed solutions than when extracting the aliphatic hydroxyamine feed solutions. Consequently, from the standpoints of both chemical separation and corrosion the aniline derivative feed solutions appear to be more desirable than either the pure hydrofluoric acid solutions or the aliphatic hydroxyamine solutions.

The separation factor and per cent transfer trends for extracting the amine feed solutions 11 to 15, inclusive, with various organic solvents were similar to those reported above for extracting the amine-free hydrofluoric acid solutions of niobium and tantalum. The ketones were the most effective organic class of compounds although the esters, organic phosphates and alcohols also yielded favorable separation factors and mass transfer values. The hydrocarbons do not appear to extract either tantalum or niobium from these amine feed solutions while Primene 81-T causes considerable extraction of material by any organic phase.

Upon comparison of the results for extracting amine feed solutions 11, 13 and 14 it appears that for the same organic phase the tantalum-niobium separation factors increased progressively for the following amines: m-tolyl diethanolamine, phenyl ethyl ethanolamine and phenyl diethanolamine. The reverse trends resulted for mass transfer to the organic phase. From the data for extractions 58, 44 and 60 or amine feed solutions 11, 13 and 14, where diethyl ketone constituted the organic phase, it can be seen that the tantalum-niobium separation factors were 358, 506 and 657, respectively, while the corresponding mass transfer to the organic phase on an oxide basis was 40.6, 38.8 and 35.0 per cent. Comparison of the data for extracting amine feed solutions 12 and 15 indicated that in all corresponding extraction the tantalum-niobium separation factor was highest for the amine feed solution containing phenyl diethanolamine.

The effect of the initial aqueous phase concentration can be observed by comparing the data for extracting amine feed solutions 11 and 12 and amine feed solutions 14 and 15. It is apparent that increasing the concentration of tantalum, niobium and amine salts in the initial aqueous phase resulted in an increase in the mass transfer to the organic phase while decreasing the tantalum-niobium separation factor. The data obtained from extracting amine feed solution 12 with different volume ratios of organic phase to aqueous phase indicate that the larger relative volume of organic phase to aqueous phase not only increases the mass transfer to the organic phase but also the tantalum-niobium separation factor. The use of these aromatic hydroxyamine feed solutions appears to be practical for the separation of tantalum from niobium.

Extraction of the potassium hydroxide solution of niobium and tantalum

In the columbite-tantalite ore treatment section it was stated that the earth acids were soluble in potassium hydroxide solution. A slightly basic solution containing the potassium salts of niobium and tantalum should not react with glass to any appreciable extent. Consequently, extraction of this system was investigated as a possible technique for separating niobium and tantalum.

A basic feed solution was prepared by dissolving the earth acids in excess potassium hydroxide. This feed solution had a pH value above 14 and contained the equivalent of about 65 grams per liter of combined niobium and tantalum pentoxides. The titration of this basic solution with standard hydrochloric acid employing phenolphthalein as the indicator gave a base concentration equivalent to 1.63 moles per liter. Since niobium and tantalum partially precipitated during this tritration, some of the hydrochloric acid must have reacted with the potassium niobate and tantalate.

This potassium hydroxide solution of niobium and tantalum could not be precipitated by addition of ammonium hydroxide. However, it was precipitated immediately by the addition of acids such as hydrochloric, sulfuric, nitric, acetic, butyric, propionic, oxalic, maleic, tartaric and salicylic in excess. It was also precipitated by ethyl alcohol, ethylenediamine, diethanolamine, diethylaminoethanol, sodium hydroxide and sodium chloride. Malic acid precipitated the solution at a pH of about 9 while citric acid (36) even in sufficient excess to give a pH of about 4 did not form a precipitate.

Many single stage extractions were carried out directly on the potassium hydroxide solution of niobium and tantalum. It was reported that all the organic compounds tested, which included ketones, alcohols, amines, ethers, esters, hydrocarbons and organic phosphates, extracted no detectable amounts of niobium or tantalum (36). However, when citric acid was added to this basic solution to neutralize it to a pH of below

7, a small amount of material was extracted by certain organic liquids. The tantalum and niobium were precipitated from the equilibrium product phases by addition of hydrofluoric acid followed by ammonium hydroxide. Without first adding the hydrofluoric acid the ammonium hydroxide will not precipitate the niobium and tantalum from a citric acid solution. It is presumed that the hydrofluoric acid destroys the citric acid complex which is stable in the presence of only ammonium hydroxide.

In a typical experiment the initial aqueous phase was prepared by adding 7.0 grams of citric acid to 20.0 milliliters of the basic feed solution. The pH of the resulting aqueous solution buffered at about 4.0. Extraction of this aqueous phase with an equal volume of a 25 volume per cent solution of Primene JM-T in methyl ethyl ketone resulted in a mass transfer to the organic phase of 9.4 per cent in terms of oxides. The product from the organic phase was 44 per cent tantalum oxide while the product from the aqueous phase was 55.0 per cent tantalum oxide. The tantalum-niobium separation factor was 1.58 for this extraction.

It is apparent from these data that for the extraction of this citric acid-potassium columbate and tantalate solution the niobium favored the organic phase while tantalum preferred the aqueous phase. Several other extractions of this aqueous feed solution showed similar trends. It is apparent that these phase preferences are opposite to those reported for extractions of the hydrofluoric acid or hydrofluoric acid-amine salt solutions. An extensive extraction study was not carried out on these basic or citric acid solutions because of the seemingly low mass transfers and separation factors which resulted from these preliminary investigations.

Multiple-contact Batch Extraction Tests

It is apparent from the data for the single stage extractions of the stock solution and its various water dilutions that a great number of common water-immiscible organic compounds separate tantalum from niobium when these elements are together in a hydrofluoric acid solution. It was observed that essentially niobium-free tantalum could easily be produced in a single stage extraction but that the preparation of tantalum-free niobium would require a series of extractions. Consequently, a number of separate multiple-contact batch extraction tests were carried out in an effort to prepare tantalum-free niobium with a high recovery. All percentages for mass transfer and recovery of material were calculated on the basis of the total oxide weight present in the initial aqueous phase. As discussed in a previous section, niobium containing less than 300 ppm tantalum is considered to be spectrographically free of tantalum while tantalum containing less than 50 ppm niobium is considered to be spectrographically free of niobium. The conditions and results of

these batch extraction tests appear below.

Batch extraction test 1

In this batch extraction test the hydrofluoric acid stock solution constituted the starting aqueous phase while di-isopropyl ketone was the organic phase. After four successive extractions of the aqueous phase with equal volumes of pure di-isopropyl ketone, greater than 95 per cent of the starting niobium oxide remained in the aqueous phase. This niobium oxide product from the aqueous phase analyzed less than 300 ppm tantalum. The organic product phase from the first of the four contacts contained about 70 per cent of all of the tantalum. This first portion of organic was scrubbed twice with a 0.77 molar hydrofluoric acid aqueous solution. For each of these two extractions only one volume of the aqueous phase was used to 10 volumes of the organic phase. This resulted in 50 per cent of the original tantalum, analyzing spectrographically free of niobium, remaining in the organic phase. However, had all four portions of the organic phase been combined without further treatment, it was calculated that the resulting tantalum would have had a purity of greater than 90 per cent.

Batch extraction test 2

In the second batch extraction test the 22 per cent hydrofluoric acid stock solution was contacted with five successive equal volume portions of pure di-isopropyl ketone. In each extraction the oxide recovered from the organic phase analyzed greater than 99.8 per cent tantalum oxide with respect to the sum of the combined tantalum and niobium oxides. Furthermore, the total extracted oxide from the five contacts represented a 68 per cent recovery of the tantalum oxide originally present in the aqueous phase. As the extractions progressed, the amount of tantalum transferred to the organic phase steadily decreased so that the fifth organic contact resulted in a transfer of only 1.9 per cent of the initial weight of combined oxides. After the fifth extraction, the aqueous phase still contained 25.9 per cent tantalum oxide and 74.1 per cent niobium oxide. It was determined that a rapid decrease in the concentration of fluoride ion in the equilibrium organic phase paralleled the decrease in the transfer of material. A very large number of such extractions would be required for complete removal of tantalum unless more hydrofluoric acid were added to the system. Tantalum spectrographically free of niobium was prepared by extracting a portion of the organic phase from the first contact with three separate portions of a 0.77 molar hydrofluoric acid aqueous solution. The relative volumes for these back-extractions were 10 volumes of organic to one volume of aqueous.

Batch extraction test 3

The third batch extraction test employed the 22 per cent stock

solution as the initial aqueous phase and virgin tributyl phosphate as the organic phase. This aqueous phase was given two successive contacts with equal volumes of the tributyl phosphate. The residual aqueous phase contained 88 per cent of the original niobium oxide with less than 300 ppm tantalum oxide. Two back-extractions of the first equilibrium organic phase with a 0.72 molar hydrofluoric acid solution resulted in a 92 per cent recovery of the original tantalum oxide containing less than 0.40 per cent niobium oxide. The relative volumes for these back-extractions were also 10 volumes of the organic phase to one volume of the aqueous phase. One more such back-extraction would probably have yielded spectrographically pure tantalum.

Batch extraction test 4

In the fourth batch extraction test the 22 per cent stock solution was contacted three separate times with diethyl ketone. The equilibrium organic phase from the first contact contained about 41 per cent of the total starting oxide weight and analyzed 0.12 per cent niobium oxide. In the second organic contact 8.8 per cent of the total starting oxide weight was extracted and an analysis showed it to contain 0.35 per cent niobium oxide. Combination of these two organic portions resulted in about a 96 per cent recovery of the total tantalum oxide which analyzed about 0.15 per cent niobium oxide. Since the aqueous phase product after these two extractions with diethyl ketone still contained about 3.7 per cent tantalum oxide a third extraction with diethyl ketone was made. This extraction resulted in the transfer of another 1.8 per cent of the total starting oxide weight to the third portion of the organic. This portion analyzed about 75 per cent tantalum oxide. The residual aqueous phase product contained better than 99 per cent of the starting weight of niobium oxide and analyzed approximately 1.0 per cent tantalum oxide. Further contacts of this aqueous phase with diethyl ketone would probably have yielded pure niobium.

Batch extraction test 5

It is apparent from batch extraction test 4 that two diethyl ketone extractions of the 22 per cent stock solution yielded a good recovery of high purity tantalum. Since several more extractions with this ketone are necessary for producing pure niobium oxide, the use of other organic solvents for the third contact of the aqueous phase were investigated. These investigations constitute batch extraction tests 5 and 6.

In batch extraction test 5 the two contacts of the 22 per cent stock solution with diethyl ketone described in batch extraction 4 were carried out. An equal volume of pure tributyl phosphate was employed for the third extraction of the aqueous phase. This tributyl phosphate contact extracted 11 per cent of the total starting oxide weight which analyzed about 14 per cent tantalum oxide and 86 per cent niobium oxide.

The niobium oxide in the residual aqueous phase contained less than 300 ppm tantalum oxide.

It is apparent that these three separate extractions of the aqueous solution yielded three niobium-tantalum fractions. One fraction contained 95 per cent of the total tantalum oxide weight analyzing only 0.15 per cent niobium oxide while a second fraction contained about 80 per cent of the total niobium oxide weight spectrographically free of tantalum. The third or intermediate fraction was primarily niobium oxide and contained 11 per cent of the total initial oxide weight.

Batch extraction test 6

In an attempt to decrease the oxide weight of the intermediate fraction while maintaining the high purity of niobium in the final aqueous product phase, an equal volume of isophorone was employed for the third extraction of the aqueous phase. This resulted in transfer of 2.3 per cent of the initial oxide weight to the organic phase. The material transferred gave a product which analyzed about 73 per cent tantalum oxide and 27 per cent niobium oxide. The equilibrium aqueous phase contained about 99 per cent of the total niobium which analyzed less than 300 ppm tantalum. It is apparent from this batch extraction test that 99 per cent of the niobium and 96 per cent of the tantalum were recovered in high relative purity.

Batch extraction test 7

In this batch extraction test, two similar contacts of the 22 per cent stock solution with diethyl ketone as reported in batch extraction 4 and also employed in batch extractions 5 and 6 were carried out. The single stage extraction data on the hydrofluoric acid solution of niobium and tantalum indicated that the presence of excess hydrofluoric acid increased the extraction by the organic phase. Consequently, in batch extraction test 7 the base equivalent of the aqueous phase, which after the second diethyl ketone extraction was 2.3 equivalents per liter, was changed to a value of 3.0 equivalents per liter by addition of hydrofluoric acid. This aqueous solution was then extracted with an equal volume of diethyl ketone.

The product from this third ketone extraction contained about 2.3 per cent of the total starting oxide weight and it analyzed about 75 per cent tantalum oxide and 25 per cent niobium oxide. The residual aqueous product phase contained about 99 per cent of the total niobium contaminated by less than 300 ppm tantalum. It is apparent that the addition of 0.7 of an equivalent per liter of hydrofluoric acid followed by extraction with diethyl ketone gave the same effects as the third extraction with isophorone reported in batch extraction test 6.

Two other batch extraction tests were carried out in which 1.7 and 2.7 equivalents per liter of hydrofluoric acid were added to the aqueous phase before the third extraction with diethyl ketone. The aqueous product phases from these third diethyl ketone extractions contained niobium contaminated with less than 300 ppm tantalum in either case. When 1.7 equivalents of hydrofluoric acid was added, about 97 per cent of the niobium oxide was recovered in the highly purified state while for the addition of 2.7 equivalents per liter only about 94 per cent was recovered. It is evident that these slight increases in hydrofluoric acid concentration decreased the recovery of purified niobium. However, the purity of the niobium prepared with the higher hydrofluoric acid concentration was possibly greater, but the analytical method employed was not sensitive below 300 ppm tantalum.

It is apparent from multiple-contact batch extraction tests 6 and 7 that in a three stage extraction of the 22 per cent stock solution, 99 per cent of the niobium as oxide spectrographically free of tantalum and 96 per cent of the tantalum as oxide containing only 0.15 per cent niobium oxide were recovered. The initial mixture contained about 48 per cent niobium oxide and 52 per cent tantalum oxide. The third or intermediate fraction which constituted only 2.3 per cent of the initial total oxide weight and was mainly tantalum, could be allowed to accumulate in large scale operations and then given a special processing. However, if the intermediate fraction were added to the high purity tantalum fraction, the resulting mixture would contain essentially 100 per cent of the tantalum with a purity of about 99 per cent relative to niobium. The purity of such a mixture could probably be increased somewhat by varying further the conditons for the third extraction of the aqueous phase.

The conditions for the quantitative separation of tantalum from niobium have been developed for their nearly equal weight mixtures. However, the same general conditions should apply for separating any composition of these two elements. As long as the concentration of free hydrofluoric acid is kept very low, only small relative amounts of niobium are extracted by diethyl ketone. If the earth acids are dissolved in a minimum amount of hydrofluoric acid and then diluted with water, several extractions of this aqueous mixture with organic solvents such as diethyl ketone should produce essentially a quantitative recovery of pure tantalum and niobium. It is believed that these extractions could readily be developed to afford a convenient analytical method for separating tantalum from niobium.

If a suitable material of construction were available, this hydrofluoric acid system could be used in a countercurrent extractor for the continuous separation of tantalum from niobium. A column fabricated from a plastic material such as polyethylene would withstand the attack of this acid fluoride solution. However, the construction and operation of

such an extractor would require some development work. The single stage data from the extraction of the stock solution indicated that about 5 to 10 stages should be sufficient for a quantitative separation of tantalum from niobium at these high concentrations. This extraction would require such organic compounds as diethyl ketone, hexone, isophorone, tributyl phosphate or methyl isopropyl ketone although many other solvents would suffice. The separation of niobium and tantalum on a large scale by liquid-liquid extraction would probably be a very simple process if a suitable extractor were available.

Multistage Extractions

The single stage and batch extraction data indicate that many organic solvents extract high purity tantalum from a hydrofluoric acid solution containing niobium and tantalum. Under these conditions only a few stages would probably be required for a quantitative separation. It was also noted from the single stage extraction data that tantalum could be easily extracted from an amine-hydrofluoric acid salt solution containing niobium and tantalum. The addition of amine markedly reduced the attack of the solution on glass. Consequently, these amine aqueous solutions were used as the feed for three separate countercurrent multistage extractions for separating tantalum from niobium. The extractor shown in Figure 1 was used in each case.

Extraction 1

The amine feed solution 11 whose composition is given in Table 5 constituted the aqueous feed for this multistage extraction while pure diethyl ketone was the introduced organic phase. The aqueous scrub solution was diluted hydrofluoric acid which had been saturated with phenyl ethyl ethanolamine giving a fluoride salt concentration of about 0.5 molar and a pH value of about 4. Only 10 stages of the 20 stage extractor were used for this extraction. For each cycle of operation there was added 10.0 milliliters of the aqueous feed solution at stage 7, 5.0 milliliters of the aqueous scrub solution at stage 10 and 30 milliliters of diethyl ketone at stage 1.

The product phases for every fifth cycle of operation were analyzed for total oxide content and for relative percentages of niobium and tantalum oxides. These analyses indicated that about 20 cycles were required to reach essentially steady state conditions. After 55 complete cycles the process was discontinued, the liquids collected from the stages and oxide analyses carried out on both phases from each stage. The results of these stagewise analyses appear in Table 7.

The data from the cycle analyses showed that tantalum was not

Table 7

Stagewise Data for the First Niobium and Tantalum Multistage Extraction

Stage no.	Organic phase		Aqueous phase	
	Grams oxide/ liter	Per cent Nb_2O_5	Grams oxide/ liter	Per cent Nb_2O_5
1	0.12	*	37.7	> 99.97
2	0.038	*	36.1	99.97
3	0.97	*	37.5	99.1
4	1.20	*	38.4	97.5
5	2.24	1.42	40.2	90.0
6	5.27	0.50	47.0	72.3
7	19.8	0.24	51.2	64.0
8	18.8	0.17	47.2	1.78
9	15.8	0.030	40.9	0.080
10	19.0	0.054	10.8	0.84

*Insufficient sample for analysis by x-ray fluorescence; per cent Nb_2O_5 outside range for the spectrographic technique employed. Values estimated at above 2.5 per cent Nb_2O_5.

detected in the niobium of the aqueous product although the lower limit of detection of tantalum in niobium by the spectrographic method employed was about 300 ppm. This high purity of the niobium product is substantiated by the data for the aqueous phase of stages one and two in the stagewise analyses appearing in Table 7. It can be seen in this table that these niobium oxide samples were 99.97 per cent or better in relation to tantalum.

Analyses of the cycle product phases showed that for the first 50 cycles of operation only about 100 ppm of niobium oxide was present in the tantalum oxide from the organic product. However, the stagewise data indicate that the oxide recovered from the organic product phase from stage 10 should have contained 0.054 per cent (540 ppm) niobium oxide. A new supply of aqueous scrub was employed for the last few cycles of operation and it is possible that this scrub contained a small amount of niobium. A slight contamination of the scrub with niobium would also explain the lower percentages of niobium in both phases in stage 9 with higher niobium percentages in stage 10. Since this laboratory is also used for other problems involving these elements, this contamination is conceivable.

The data in Table 7 show that the maximum oxide concentrations of both the aqueous and the organic phases were in stage 7, the feed stage. It is also apparent that very little material was extracted into the organic phase in stages one and two. The over-all material balance, based on average analyses, concentrations and volumes of product indicated that the organic product phase delivered from stage 10 and the aqueous product phase delivered from stage one contained about 51 per cent and 49 per cent, respectively, of the total weight of tantalum and niobium oxides.

Figure 10 shows the variation of the oxide composition, expressed as niobium pentoxide percentage, with stage number for both the organic and aqueous phases. It is apparent from the data that very little niobium transferred to the organic phase in any stage. Since the large variation in niobium percentage in the aqueous phase is due mainly to the distribution of tantalum to the organic phase, the separation then depends essentially on the selective transfer of tantalum. Consequently, the prime operation factor in this separation is the organic scrubbing of the aqueous feed solution. It was observed, therefore, that in this extraction employing an approximately 50-50 mixture of niobium and tantalum that there was a quantitative separation into a tantalum fraction containing 100 ppm niobium and a niobium fraction spectrographically free of tantalum.

Extraction 2

The results from the first multistage extraction indicated that a

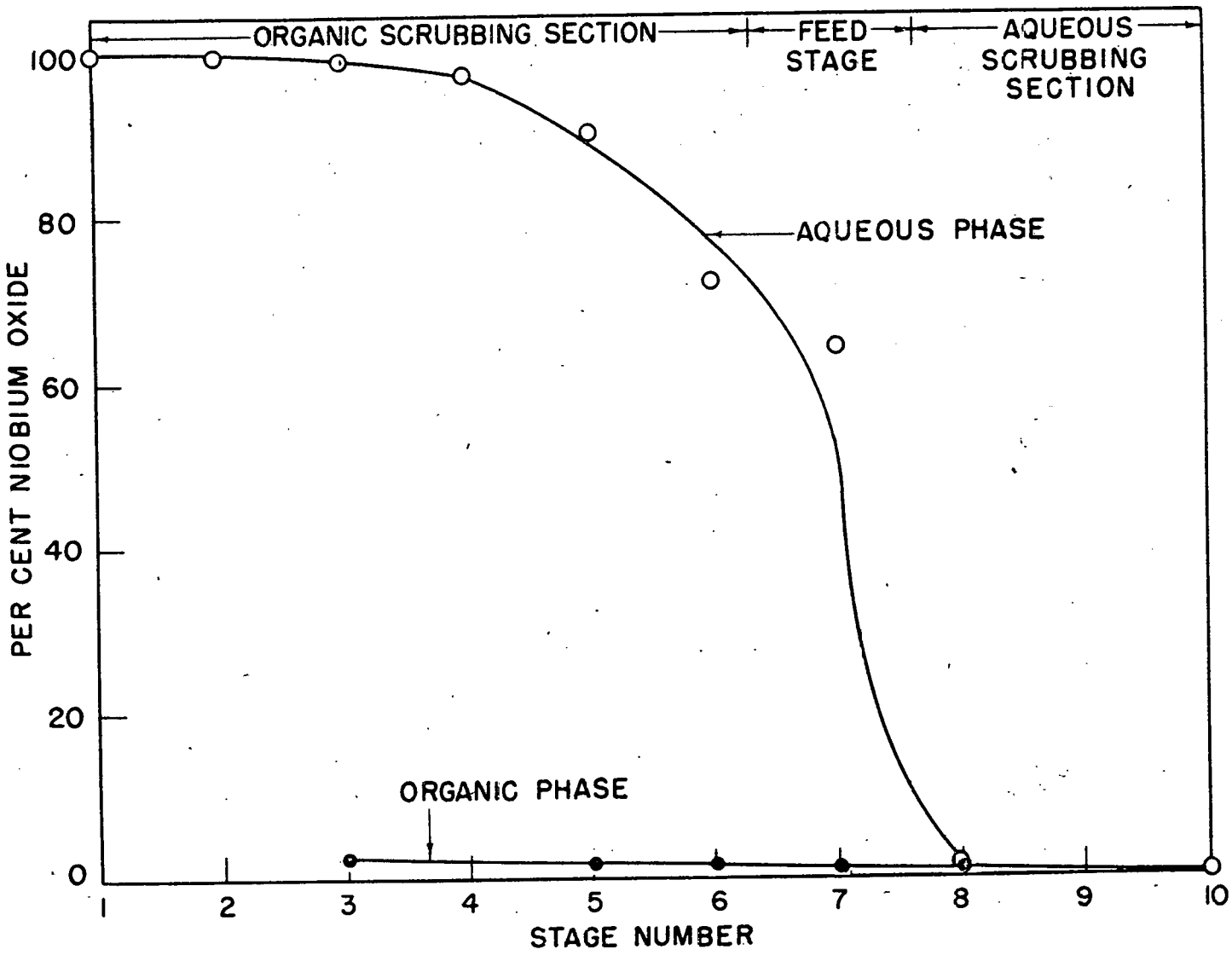

Figure 10 - Niobium Oxide Percentages in the Equilibrium Liquid Phases as a Function of Stage Number.

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nearly quantitative separation of tantalum and niobium resulted when extracting their phenyl ethyl ethanolamine-hydrofluoric acid salt solution with diethyl ketone. From the data for the single stage extractions it was observed that phenyl diethanolamine was a more effective amine for obtaining this separation of niobium and tantalum. Consequently, this amine was employed for preparing the feed solution. A higher concentration of tantalum and niobium in the aqueous feed was also employed in order to increase the rate of production of tantalum and niobium. Since the tantalum-niobium separation factor decreases with an increase in concentration of niobium, tantalum and amine, 15 stages were used in this extraction.

Amine feed solution 15 (see Table 5) constituted the aqueous feed solution while diethyl ketone was the organic phase. The aqueous scrub solution was prepared by partially neutralizing a 0.50 molar hydrofluoric acid solution to a pH of 4 with phenyl diethanolamine. For each cycle of operation 10.0 milliliters of the amine feed solution, 30.0 milliliters of diethyl ketone and 5.0 milliliters of the aqueous scrub were added at stages 9, 1 and 15, respectively. The extraction process was carried out for 83 cycles although the products from every tenth cycle were analyzed. Analyses of the liquid phases in each stage were carried out after the extraction process was completed.

The cycle analyses indicated that about 40 cycles of operation were required to reach essentially steady state. These analyses showed that the niobium delivered in the aqueous product phase contained less than 300 ppm tantalum. These data were substantiated by the stagewise data which appear in Table 8. It can be noted from the data in this table that the niobium in the equilibrium aqueous phase of stages 1, 2 and 3 was spectrographically free of tantalum. Since high purity niobium was obtained in these three end stages, it is probable that the contamination of the niobium by tantalum in the aqueous product phase was considerably lower than 300 ppm, the lower limit of detection.

Analyses of the organic product phase indicated that the tantalum in this phase contained about 0.020 per cent (200 ppm) niobium on the oxide basis. It can be noted from the stagewise data for the organic phase that a minimum for the per cent niobium in tantalum occurred in stage 13. In this stage the tantalum was spectrographically free of niobium since it contained less than 50 ppm. It appears that the aqueous scrub solution, introduced at stage 15, must have been contaminated by niobium. This would also explain the relatively high values for the niobium oxide percentages in the equilibrium aqueous phase in the aqueous scrubbing section of the extractor.

A qualitative analysis of this amine scrub solution indicated that moderate to strong amounts of both niobium and tantalum were present. In order to determine the source of this contamination, qualitative analyses

Table 8

Stagewise Data for the Second Niobium and Tantalum Multistage Extraction

Stage no.	Organic phase			Aqueous phase		
	Vol. (ml.)	Grams oxide/ liter	Per cent Nb_2O_5	Vol. (ml.)	Grams oxide/ liter	Per cent Nb_2O_5
1	31.5	.096	*	11.0	119	> 99.97
2	31.8	.044	*	12.8	113	>99.97
3	32.0	.204	*	13.3	113	>99.97
4	33.2	.760	*	12.2	110	99.3
5	31.0	2.26	1.25	11.9	112	98.5
6	31.1	5.96	0.64	12.7	112	96.5
7	32.6	12.2	0.50	13.8	123	89.7
8	32.8	25.2	0.51	16.2	131	73.6
9	33.0	52.5	0.60	16.0	149	55.5
10	34.8	50.7	0.038	5.9	68.0	3.47
11	36.2	52.7	0.007	5.7	58.6	0.27
12	35.7	49.7	0.005	5.8	66.4	0.14
13	34.4	50.1	< 0.005	6.0	54.5	0.14
14	34.5	50.1	0.017	5.9	51.5	0.14
15	31.2	45.7	0.019	5.7	47.1	0.18

*Refer to Table 7.

were carried out on the hydrofluoric acid and phenyl diethanolamine which were employed in preparing this amine feed solution. The pure amine was relatively free of niobium or tantalum but the hydrofluoric acid contained moderate amounts of both. A qualitative analysis on a portion of hydrofluoric acid obtained from a new bottle indicated the absence of niobium or tantalum. Consequently, it was assumed that the hydrofluoric acid employed in preparing the amine feed solution was contaminated prior to its use in this multistage extraction. This probably also explains the contamination error observed in the first niobium-tantalum multistage extraction.

An over-all material balance based on the average analyses, concentrations and volumes of the product phases indicated that about 52 per cent of the material on an oxide basis was delivered by the organic product phase. As in the case of the first multistage extraction of niobium and tantalum, the maximum oxide concentration for both phases was in the feed stage. Very little niobium oxide was extracted by the organic phase of any stage.

The stagewise data indicated that niobium spectrographically free of tantalum could have been produced even if two stages were eliminated in the organic scrubbing section of the extractor. Had an amine scrub solution free of niobium been employed, it is apparent from the stagewise data that tantalum spectrographically free of niobium could have been obtained with two less stages in the aqueous scrubbing section of the extractor. Consequently, it is probable that when employing this system tantalum spectrographically free of niobium and niobium spectrographically free of tantlum could be produced on a continuous basis in an 11 stage extractor.

Extraction 3

In the second multistage niobium-tantalum extraction a system was indicated for preparing niobium and tantalum spectrographically free of each other on a continuing basis. The system employed for this third multistage extraction was similar to the one used in extraction two. The concentrations of amine, niobium and tantalum in the feed solution were the only variation. In preparing the feed solution only sufficient phenyl diethanolamine was added to the stock solution to give a pH of about one and a niobium-tantalum concentration equivalent to about 300 grams per liter. According to the single stage extraction data a decrease in the pH value, or amount of phenyl diethanolamine present, would increase the tantalum-niobium separation factor. On the other hand, the increase in niobium and tantalum concentration should decrease this separation factor. For either variable change the per cent mass transfer from the aqueous to the organic phase was not expected to change appreciably.

The aqueous scrub and the organic liquid employed for this multistage extraction had the same compositions as those used in the second multistage extraction. A qualitative analysis on the aqueous scrub indicated that it was free of niobium and tantalum. The flow rates and stages of introduction of all three influents and the delivery stages of both product phases were the same as employed for extraction two. The product phases from every tenth cycle of operation were analyzed for niobium and tantalum. About 30 cycles were required to essentially reach a steady state condition. After 64 cycles were completed, the extraction was discontinued. The liquids in each stage were removed, separated, and their volumes measured. They were then analyzed for niobium and tantalum content. Table 9 contains the results from these stagewise analyses.

It is apparent from the stagewise data that the organic product phase, delivered from stage 15, contained tantalum spectrographically free of niobium (or less than 50 ppm). All the equilibrium portions of the organic phase in stages 10 to 15, inclusive, were free of niobium. The portions of the equilibrium aqueous phase from stages 12 to 15, inclusive, were also free of niobium. This indicated that under the conditions of the extraction not more than three stages in the aqueous scrubbing section of the extractor would be required to obtain tantalum spectrographically free of niobium.

These stagewise data also show that the aqueous product phase, delivered from stage one, contained the equivalent of 98.7 per cent niobium oxide and 1.3 per cent tantalum oxide. This indicates that with the flow rates employed, more stages are required in the organic scrubbing section to produce high purity niobium. An over-all material balance based on average volumes and analyses indicated that about 50 per cent of the oxide by weight was delivered by each product phase. Evidently the decrease in the amount of amine in the system resulted in a decrease in the per cent of the material transferred to the organic phase. It is probable that an increase of organic volume to about 33 to 35 milliliters per cycle would have yielded the desired oxide split with the number of stages employed. The data from multistage extraction two showed that the addition of more amine to form a saturated solution yielded the proper oxide split by weight.

This third multistage extraction showed that tantalum spectrographically free of niobium could be produced on a continuous basis from a concentrated niobium and tantalum solution. It was also observed that the effect of decreasing amine concentration must be overcome by increasing the relative organic phase flow rate. It is believed that the conditions employed in this extraction could easily be adjusted to obtain at the same time both niobium and tantalum spectrographically free of each other on a continuous basis.

Table 9

Stagewise Data for the Third Niobium and Tantalum Multistage Extraction

Stage no.	Organic phase			Aqueous phase		
	Vol. (ml.)	Grams oxide/ liter	Per cent Nb_2O_3	Vol. (ml.)	Grams oxide/ liter	Per cent Nb_2O_5
1	34.0	0.253	*	12.5	129	98.7
2	33.8	1.17	*	13.8	120	97.3
3	31.5	1.39	*	13.4	123	93.9
4	33.8	3.06	*	13.0	125	93.0
5	34.2	3.40	1.8	13.5	123	92.7
6	32.8	6.70	1.0	14.0	127	86.4
7	37.0	9.60	0.70	13.9	127	84.4
8	37.0	21.2	0.60	14.5	140	72.2
9	34.3	59.5	0.48	15.0	155	58.2
10	30.8	59.4	< 0.005	6.2	85.4	4.5
11	31.0	57.4	< 0.005	6.6	67.0	0.058
12	29.6	60.4	< 0.005	6.4	61.0	< 0.005
13	29.8	54.9	< 0.005	6.5	52.2	< 0.005
14	29.0	57.0	< 0.005	6.5	43.7	< 0.005
15	29.3	51.2	< 0.005	6.3	35.0	< 0.005

*Refer to Table 7.

These three multistage extractions indicated the applicability of countercurrent extraction for continuously preparing spectrographically pure niobium and tantalum. The industrial application of such a process entails the recovery and recycling of the organic solvent and amines. Small scale experiments indicated that about two equal volume contacts of the organic phase with water will back extract almost all of the niobium and tantalum. It was also determined that from 60 to 80 per cent of the amine fed to the extractor was delivered from the extractor by the organic product phase. For a continuous operation some of the amine could probably be added to the system by the influent organic phase. This would possibly eliminate recovering the amines from the organic product phase. The addition of such bases as ammonia or calcium oxide to the aqueous phase regenerates the amine which is insoluble. Consequently, the amine separates as a second layer and can be recovered by decantation.

CONCLUSIONS

Ore Processing

The niobium-tantalum fraction in a columbite-tantalite ore was rendered soluble by carrying out a series of treatments starting with a caustic fusion. A sodium hydroxide leach of the fusion product followed by a nitric or hydrochloric acid leach of the residue removed most of the common impurities. The remaining insoluble fraction which was essentially niobium and tantalum acid oxides was dissolved in either hydrofluoric acid or potassium hydroxide.

Single Stage Extractions

a. Many water immiscible organic solvents preferentially extract tantalum from a hydrofluoric acid solution containing tantalum and niobium. Tantalum essentially free of niobium was produced in a single stage extraction while the preparation of niobium free of tantalum required a series of extractions. As a general class, the ketones appeared to be the most effective for obtaining pure tantalum although many alcohols, aldehydes, amines, phosphites, phosphates, ethers, esters and mixed organic solvents were also decidedly effective.

b. An increase in the concentration of free hydrofluoric acid decreased the niobium-tantalum separation factor but increased the mass transfer from the aqueous phase to the organic phase.

c. The dilution of the hydrofluoric acid solution of niobium and tantalum with water resulted in an increased preferred extractability of tantalum.

d. Certain aliphatic and aromatic hydroxyamines form a stable partially or completely neutralized solution when added to the hydrofluoric acid solution of niobium and tantalum. These amine systems did not react appreciably with glass.

e. The transfers of niobium and tantalum to the organic phase and the tantalum-niobium separation factors were generally quite low when their hydrofluoric acid solutions were neutralized with the aliphatic hydroxyamines and then extracted with pure organic solvents. The presence of Primene JM-T or Primene 81-T in the organic solvent increased considerably the mass transfer to the organic phase while not affecting appreciably the tantalum-niobium separation factors.

f. The presence of an inert diluent in the organic phase decreased the mass transfer as well as the tantalum-niobium separation factor.

g. Extractions of the hydrofluoric acid solution which were neutralized with the aromatic hydroxyamines yielded high purity tantalum in the equilibrium organic phase, appreciable mass transfer and favorable tantalum-niobium separation factors. The same general trends for the organic solvents that were reported when extracting the amine-free hydrofluoric acid solution of niobium and tantalum were observed here. Phenyl diethanolamine appeared to be the most effective aromatic amine for neutralizing the excess hydrofluoric acid from both a cost and chemical separation viewpoint.

h. The extraction of a potassium hydroxide solution of the earth acids which had been neutralized to a pH of 4 with citric acid indicated that niobium was preferentially extracted by the organic phase. The amount of material extracted by the organic phase and the tantalum-niobium separation factor in this system were much smaller than those observed with the hydrofluoric acid system of niobium and tantalum.

Multiple-Contact Batch Extractions

a. A series of batch extraction tests employing the hydrofluoric acid solution of niobium and tantalum were carried out. In three contacts of the 22 per cent stock solution with diethyl ketone 96 per cent of the total tantalum oxide containing 0.15 per cent niobium oxide and 99 per cent of the total niobium oxide spectrographically free of tantalum were obtained. The intermediate or third fraction which was primarily tantalum contained 3.2 per cent of the total weight as oxide. A small amount of hydrofluoric acid solution was added to the aqueous phase after the second extraction with diethyl ketone.

b. Two extractions of the 22 per cent stock solution with diethyl ketone and a third extraction with isophorone without the addition of hydrofluoric acid yielded the same three fractions reported in a (above).

c. The three stage extraction of the 22 per cent stock solution with diethyl ketone resulted in a quantitative recovery of the tantalum with a 99 per cent purity relative to niobium and 99 per cent recovery of niobium spectrographically free of tantalum.

d. A procedure was presented whereby any mixture of niobium and tantalum could probably be effectively separated into its pure components.

e. A countercurrent extractor consisting of from about 5 to 10 equilibrium stages should effectively separate niobium and tantalum on a continuing basis by employing one of the many organic solvents tested for the extraction of a hydrofluoric acid solution of niobium and tantalum.

Multistage Extractions

a. Three multistage extractions of the aromatic hydroxyamine neutralized hydrofluoric acid solution of niobium and tantalum were carried out to prepare the spectrographically pure salts.

b. Niobium spectrographically free of tantalum and tantalum containing about 100 ppm niobium were prepared on a continuing basis in 10 stages. The feed solution was saturated with phenyl ethyl ethanolamine and contained the equivalent of about 95 grams of niobium and tantalum oxide per liter.

c. In 15 stages niobium spectrographically free of tantalum and tantalum containing about 200 ppm niobium were obtained on a continuing basis. The feed solution was saturated with phenyl diethanolamine and contained the equivalent of about 260 grams of niobium and tantalum oxides per liter. Stagewise analyses and a qualitative analyses of the aqueous scrub indicated that this scrub solution was contaminated with niobium. The tantalum would probably have been spectrographically free of niobium if this contamination had not existed.

d. Tantalum spectrographically free of niobium and niobium containing 1.3 per cent tantalum oxide were obtained in 15 stages on a continuing basis. The feed solution was neutralized to a pH of one by phenyl diethanolamine and contained the equivalent of about 300 grams of niobium and tantalum oxides per liter.

e. Ten to 15 stages was sufficient for a quantitative separation of both tantalum and niobium spectrographically free of each other on a continuing basis when they were fed to the extractor together in an amine-hydrofluoric acid solution.

SUMMARY

The tantalum and niobium mixture which contained about equal weights of each element was obtained by processing a columbite-tantalum ore. A stable aqueous solution, or stock solution, containing the equivalent of 517 grams of tantalum and niobium pentoxides per liter was obtained by dissolving the mixed earth acids in concentrated excess hydrofluoric acid. About six moles of hydrofluoric acid per mole of this niobium-tantalum mixture were required to obtain a stable aqueous solution. Single stage extractions of this stock solution and its various water dilutions with many organic solvents indicated that tantalum was always preferentially extracted. As a general organic class, the ketones were most effective in obtaining the niobium-tantalum separation. However, many alcohols, amines, aldehydes, ethers, esters, organic phosphates, organic phosphites and mixed organic solvents also extracted appreciable quantities of high purity tantalum. Several of the organic solvents in a single stage extraction of a 22 per cent aqueous stock solution employing equal volumes of the two phases extracted greater than 50 per cent of the tantalum which analyzed less than one per cent niobium. Included in this group were triethyl citrate, diethyl ketone, heptanone-2, isophorone, mesityl oxide, methyl-n-hexyl ketone, methyl isobutyl ketone, methyl isopropyl ketone, tri-2-ethylhexyl phosphite and a 5.0 volume per cent solution of Primene JM-T in diethyl ketone. Tantalum-niobium separation factors as high as 4180 were obtained from these single stage extractions.

As the water dilution of the stock solution was increased, the tantalum-niobium separation factors and purity of the separated tantalum also increased while the mass transfer of niobium and tantalum to the organic phase decreased. A series of extractions was carried out in which diethyl ketone was the organic phase while the aqueous phase contained various ratios of hydrofluoric acid concentration to niobium plus tantalum concentration. It was observed that a decrease in the amount of excess hydrofluoric acid decreased the mass transfer to the organic phase and gave increased tantalum-niobium separation factors. Very little preference in the extractability of tantalum was evident when a large excess of hydrofluoric acid was present. It was proposed that in the presence of small amounts of free hydrofluoric acid the niobium and tantalum species in the aqueous solution are different while they approach similarity as the excess acid is increased.

A series of multiple-contact batch extraction tests was carried out on the 22 per cent stock solution. Three successive equal volume extractions of this aqueous solution with pure diethyl ketone resulted in a recovery of 99 per cent of the niobium spectrographically free of tantalum and a 96 per cent recovery of the tantalum containing 0.15 per cent niobium oxide. The intermediate fraction, which was mainly tantalum,

constituted 2.3 per cent of the initial total oxide weight. It was necessary to add a small amount of hydrofluoric acid to the system before making this third extraction with diethyl ketone. If isophorone were used in place of diethyl ketone for this third extraction, the same results were obtained without this latter addition of hydrofluoric acid. It is believed that this multiple-contact extraction process could be readily developed to afford convenient analytical and commercial methods for separating tantalum from niobium.

Because of the highly corrosive nature of acid fluoride solutions toward glass equipment, other liquid-liquid systems were investigated for separating niobium and tantalum. A potassium hydroxide solution of the niobium and tantalum earth acids was neutralized with citric acid and extracted with an organic. The results indicated that niobium in this case was preferentially extracted by the organic phase. Although this system was not fully investigated, the lower values of the mass transfer to the organic phase and of the tantalum-niobium separation factor indicated that this solution was decidedly less favorable for effecting a separation of niobium from tantalum.

Aliphatic and aromatic hydroxyamines neutralized and formed a stable solution with the hydrofluoric acid solutions of niobium and tantalum. Corrosion tests indicated relatively little attack on glass by these hydrofluoric acid systems which had been neutralized with amines to a pH of 4 or more. A number of single stage extractions of these amine-neutralized solutions with various organic solvents was carried out. Tantalum was preferentially extracted by the organic phase. In general, the tantalum-niobium separation factors obtained by extracting these amine-neutralized solutions were lower than those obtained by extracting the hydrofluoric acid solutions of niobium and tantalum. The hydrofluoric acid solutions which had been neutralized by the aromatic hydroxyamines yielded much greater transfers to the organic phase and greater tantalum-niobium separation factors than the corresponding aliphatic hydroxyamine neutralized systems. In the former systems tantalum-niobium separation factors as high as 657 were obtained.

Three countercurrent multistage extractions were carried out employing diethyl ketone as the organic phase and these aromatic hydroxyamine neutralized hydrofluoric acid solutions of niobium and tantalum as the aqueous feeds. The feed solution in the first extraction was neutralized with phenyl ethyl ethanolamine and contained the equivalent of 95 grams of combined niobium and tantalum pentoxides per liter. In 10 stages, tantalum containing 100 ppm niobium and niobium spectrographically free of tantalum were delivered by the organic and aqueous product phases, respectively.

The feed solutions for the second and third multistage extractions of this series were neutralized with phenyl diethanolamine and contained the equivalent of 260 grams and 300 grams, respectively, of the combined niobium and tantalum pentoxides per liter. Fifteen stages were employed for these extractions. In the second extraction, tantalum containing 200 ppm niobium and niobium spectrographically free of tantalum were obtained. The organic phase product of the third multistage extraction contained tantalum spectrographically free of niobium while the aqueous phase product was 98.7 per cent niobium oxide and 1.3 per cent tantalum oxide. These multistage extractions indicated the practicability of countercurrent liquid-liquid extraction as a method for separating tantalum and niobium in quantity on a continuous basis.

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APPLICATION OF LIQUID-LIQUID EXTRACTION TO THE SEPARATION OF TANTALUM FROM NIOBIUM

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